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LASER PHOTOCHEMISTRY . I. PARTIAL PHOTORESOLUTION OF TRIS(ACETYLACETONATO)CHROMIUM(III) AND RELATED COMPLEXES

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An argon ion laser has been used to partially photoresolve tris(acetylacetonato)chromium(III), tris(3-nitroacetylacetonato)-chromium(III), and tris(trifluoroacetylacetonato)chromium(III). The optical rotatory dispersion and the circular dichroism spectra of the optically pure enantiomers have been determined in the wavelength range of 400-650 nm.

Only one example exists, (1) to our knowledge, in which laser beam is used to photoresolve metal complex racemates. The phenomenon of photoresolution including the asymmetric photodecomposition has long been known.(2-10) The optical resolution by right- or left-circularly polarized light has one distinctive advantage over other chemical methods of resolution in that, although the method can not in general resolve completely, it allows the determination of the circular dichroism(CD) and the optical rotatory dispersion(ORD) curves of the optically pure enantiomer. Further, the method can be applicable, especially, to so-called inner complexes which have no formal charge. The laser beams have some advantages; first, as is well known, the light intensity of laser beams can be made stronger. Secondly, we can obtain directly linearly polarized light(in the case of outer mirror type lasers) which can be transformed easily into circularly polarized light.

It is reported here that an argon ion laser has been used to photoresolve the titled complexes and that the CD and ORD curves of the optically pure enantiomers have been determined.

Experimental

The experimental arrangement used in this work is similar to that reported in the literature.(1,8,9) The light source is a NEC GLG-2023 argon ion laser operating at 514.5, 501.7, 496.5, 488.0, 476.5, or 457.9 nm(in single mode). The linearly polarized light emitted from the laser is passed through a quartz quarter-wave-plate matched for the wavelength of the light to produce circularly polarized light. Circularly polarized light is then incident on a 1 cm cell containing the solution to be irradiated. The diameter of the beam is approximately 8 mm. The ellipticity of the circularly polarized light 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. Light intensity incident on the sample solution is monitored by measuring the current induced in a photovoltaic CdS cell. The ORD spectra have been recorded on a JASCO Model ORD/UV-5 spectrometer and the CD spectra on a JASCO Model J-2 spectrometer. The complexes are prepared after the well-established methods$^{(11)}$ and the identity of the complexes are confirmed by chemical analysis. The solution to be irradiated is made to 5×10^{-3}mol/l in benzene.

Principle

The principle of photoresolution is the preferential isomerization of one enantiomer over the other, which is the mere consequence of the differential absorptivity of two enantiomers in a circularly polarized light(circular dichroism). Thus, the efficiency of the photoresolution is a function of the asymmetric factor (g) of the complex to be resolved. It is shown$^{(8)}$ that the photostationary state (pss) should yield the optical rotation

$$\theta_{pss} = \theta\, g/2 \;,$$

and the circular dichroism which is proportional to

$$(g\, \varepsilon\, c_0 d)\, g/2 \;,$$

both at the wavelength used for the photoresolution. In the above, θ is the optical rotation expected for the optically pure enantiomer whose concentration is c_0(mol/l). The parenthesized term ($g\varepsilon\, c_0 d$) is the circular dichroism which would be obtained if complete resolution is achieved.

The procedure to obtain the CD and ORD curves of the optically pure enantiomer is simply a rescaling of those observed on the partially resolved complex. The sample solution partially resolved affords directly the quantity $(g\,\varepsilon c_0 d)g/2$. As quantities ε , c_0 , and d can be known independently, we obtain asymmetric factor, g, and hence the molecular rotation, [M], and $\varepsilon_l - \varepsilon_r$ (CD), all at the wavelength used for the resolution.

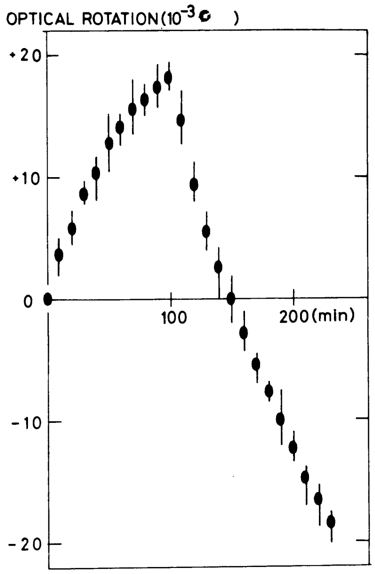

Fig. 1. The time-dependence of the photoinversion process of $Cr(acac)_3$ in benzene solution.

Results and Discussion

Figure 1 illustrates the time dependence of the photoinversion process of $Cr(acac)_3$ in benzene solution at the wavelength 514.5 nm. At time t= 100 min., the sense of the circular polarization is inverted by rotating the quarter-wave-plate through 90°. This plot clearly shows that the process of photoresolution is reversible. The fact that no measurable photodecomposition has occured is confirmed spectrophotometrically. The photostationary state reported here is reached in less than 2 hr when the incident power on the sample solution is approximately 150 mW and the solution is 1.6 cm^3(the time needed for the achievement of photostationary state is independent of the concentration of the solution if it is dilute). $Cr(acac)_3$ has been partially resolved

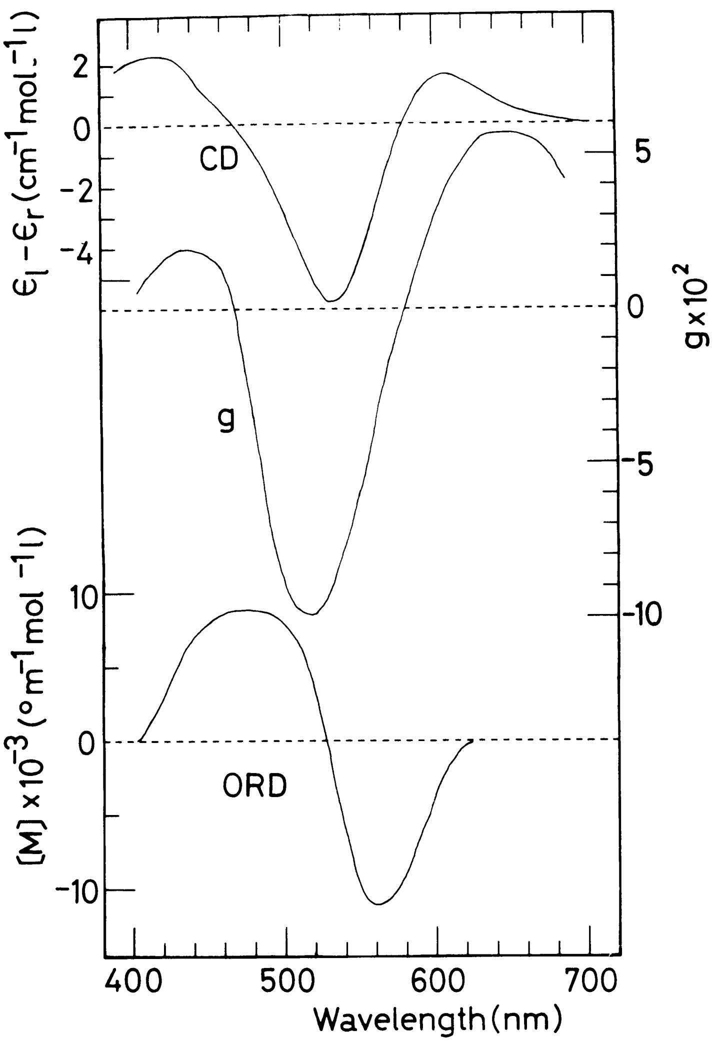

Fig. 2. The CD, ORD, and g-factor curves of the optically pure $(-)_{589}$-Cr(acac)$_3$ in 5×10^{-3} mol/l benzene solution.

by Stevenson(10) using a high-pressure mercury lamp in more than 200 hr. The ORD, CD, and asymmetric factor, g, of the optically pure $(-)_{589}$-Cr(acac)$_3$ is depicted in Fig. 2. The asymmetric factor at 514.5 nm of this complex is rather large; g $= \Delta\varepsilon/\varepsilon = 9.63 \times 10^{-2}$. This corresponds to 4.8% resolution in the present case. The result obtained in this work is a little different from that given by Stevenson in that the former is greater in absolute magnitude by some 25%. It is probable that Stevenson's result corresponds to the unsaturated(non-photo-stationary) state.

Figures 3 and 4 show the results of $(+)_{589}$-tris(3-nitroacetylacetonato)chromium(III) and $(+)_{589}$-tris(trifluoroacetylacetonato)chromium(III), respectively. We have been successful in photoresolving the following complexes; tris(3-chloroacetylacetonato)chromium(III), tris(3-bromoacetylacetonato)chromium(III) tris(3-iodoacetylacetonato)-chromium(III), and tris(hexafluoroacetylacetonato)chromium (III). In addition to Cr(acac)$_3$, all these complexes have been observed to racemize thermally because the solution partially photoresolved loses the optical activity with life-time of 2-3 weeks at room temperature. These data will be published later.

The complexes reported to be photoresolved so far, without photodecomposition, are Cr(acac)$_3$,(10) $[\mathrm{Cr(ox)_3}]^{3-}$,(8) and $[\mathrm{Cr(ox)phen_2}]^{+}$, $[\mathrm{Cr(ox)_2phen}]^{-}$, $[\mathrm{Cr(bipy)_3}]^{3+}$ and $[\mathrm{Cr(thox)_3}]^{3-}$,(1) where abbreviations are as usual. It should be noted here that all these complexes, including complexes photoresolved in this work, are observed to thermally racemize.(1,7-10) Although much more experimental investigation is necessary, we are inclined to presume that photoresolution can be effected on those complexes which racemize thermally.

We are now trying to photoresolve other tris-β-diketonates of chromium(III) and related complexes.

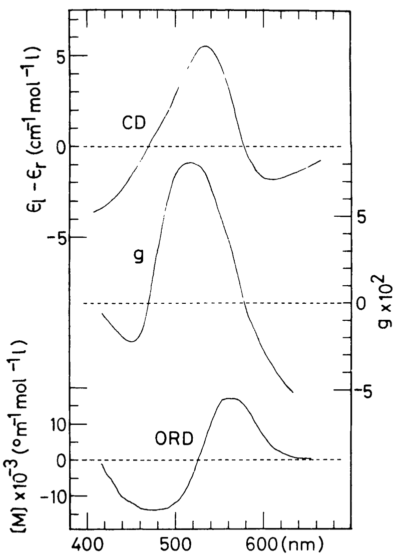

Fig. 3. The CD, ORD, and g-factor curves of $(+)_{589}$-tris(3-nitroacetylacetonato)-chromium(III) in $5x10^{-3}$ mol/l benzene solution.

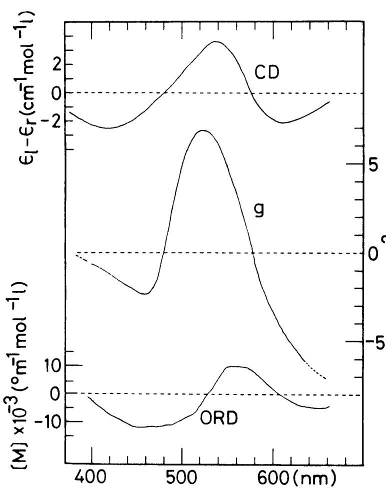

Fig. 4. The CD, ORD, and g-factor curves of $(+)_{589}$-tris(trifluoroacetyl-acetonato)chromium(III) in $5x10^{-3}$ mol/l benzene solution.

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