ppm for these highly symmetric species. Presumably changes in $\Delta\sigma_{\mathrm{local}}$ between one of these molecules and a solute of lower symmetry are at least of this order of magnitude. Also, shift changes may depend on concentration. If the actual isotropic → nematic shift is not large compared to $\Delta\sigma_{\mathrm{local}}$, the measurement of $(\sigma_{\parallel} - \sigma_{\perp})_{\mathrm{H}}$ for the solute is unreliable. Even nonequivalent protons in the same molecule might experience differences in $\Delta\sigma_{\mathrm{local}}$. Fluorine isotropic → nematic shifts may be an order of magnitude greater than $\Delta\sigma_{\mathrm{local}}$, but care is still needed in determining $(\sigma_{\parallel} - \sigma_{\perp})_{\mathrm{F}}$ because of temperature dependence of the shift (Figure 1). The actual shifts should be extrapolated to the phase-change temperature, but even then there is the effect of $\Delta\sigma_{\mathrm{local}}$ to be considered.

A. D. Buckingham, E. E. Burnell, C. A. de Lange
School of Chemistry, Bristol University
Bristol 8, England
Received April 8, 1968

Partial Photoresolution. Preliminary Studies on Some Oxalato Complexes of Chromium(III)

Sir:

We are investigating the use of circularly polarized light as a means of partially resolving a racemic mixture. We have irradiated racemic aqueous solutions of trioxalatochromate, *cis*-dioxalatodiaquochromate, and di-μ-hydroxy-tetraoxalatodichromate with right-handed circularly polarized (RHCP) light at 546 nm and observed an induction of optical activity. Unlike related earlier experiments[1-3] in which the optical activity induced in a chemical system always disappeared upon continued photolysis, the above-named systems attained an equilibrium optical activity as shown in Figures 1-3. The photolytic induction of optical activity occurs because the enantiomers of the racemic mixtures possess circular dichroisms ($\epsilon_{\mathrm{L}} - \epsilon_{\mathrm{R}}$) which are equal but opposite in sign; hence the rates of absorption of one kind of circularly polarized light are unequal. If there is a photochemical reaction at the wavelength of appreciable CD then the reaction will proceed asymmetrically, inducing optical activity into the system. Moreover, if the only photochemical reaction undergone by an isomer is inversion to its enantiomer, the effect of the circularly polarized light on the racemic mixture will be a partial resolution, a process which can be called photoresolution. The maximum extent of photoresolution is governed by the dissymmetry factor, CD/ϵ, and amounts to a few per cent for the systems we have studied. This fraction is large enough to study kinetics and determine ORD–CD curves.

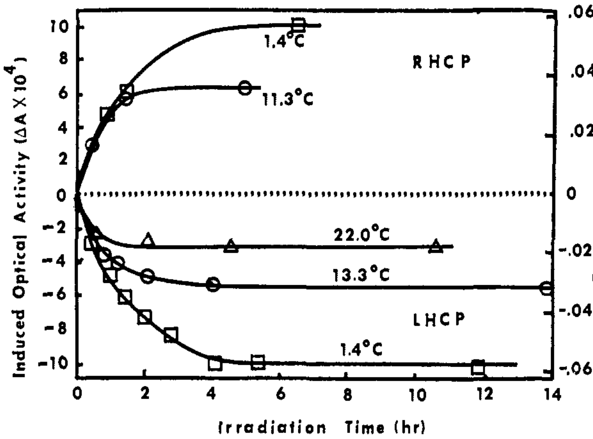


Figure 1. Photoresolution of trioxalatochromate(III), 2.6×10^{-2} *M*, in RHCP and LHCP light at 546 nm.

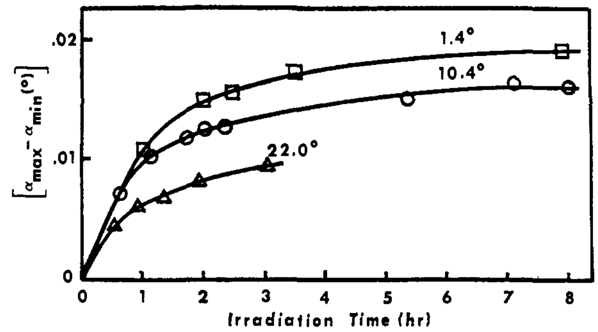


Figure 2. Optical activity induced in di-μ-hydroxy-tetraoxalatodichromate(III), 6×10^{-3} *M*, in RHCP light at 546 nm.

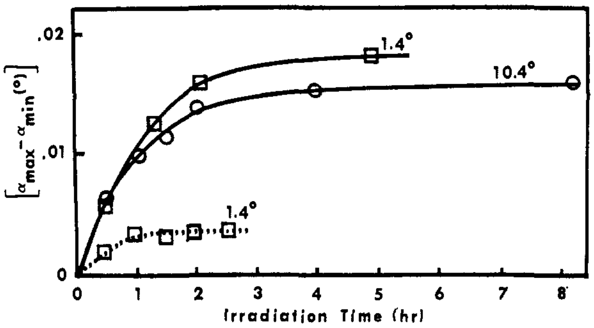


Figure 3. Optical activity induced in (———) *cis*-dioxalatodiaquochromate(III), 2.7×10^{-2} *M*, and (– – – –) *trans*-dioxalatodiaquochromate(III), 2.5×10^{-2} *M*, in RHCP at 546 nm.

For our systems, named above, there do not seem to be any irreversible photoreactions, and an equilibrium state is attained such as that shown for trioxalatochromate in Figure 1. For this system it is known that thermal racemization occurs along with the photointerconversion of enantiomers,[4] and the equilibrium state is determined by this competition. The data of Figure 1 are well represented by the integrated rate expression

$$\Delta A = [k_{\mathrm{p}}a/(k_{\mathrm{p}}b + k_{\mathrm{T}})][1 - \exp(-k_{\mathrm{p}}b - k_{\mathrm{T}})t] = \Delta A_{\mathrm{eq}}[1 - \exp(-ak_{\mathrm{p}}t/\Delta A_{\mathrm{eq}})]$$

where $\Delta A = A_{\mathrm{L}} - A_{\mathrm{R}}$, the measured difference in absorbance of solution in LHCP and RHCP light; "eq" denotes equilibrium value; a = 0.5 (concentration of solution) × (CD of + isomer); $b = \epsilon/[(\text{cell length})\cdot(\text{CD of + isomer})]$; k_{T} is the thermal racemization rate constant, and k_{p} is a photoresolution rate constant (a function of light intensity and quantum yield). Using this equation and the value for k_{T} as obtained by Spees and Adamson[4] we obtain the CD of either isomer at the irradiating wavelength. Our data yield a CD of

---

[1] W. Kuhn and E. Braun, *Naturwissenschaften*, **17**, 227 (1929).

[2] R. Tsuchida, A. Nakamura, and M. Kobayashi, *J. Chem. Soc. Japan*, **56**, 1335 (1935).

[3] R. L. Davis and R. Heggie, *J. Am. Chem. Soc.*, **57**, 377 (1935).

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

2.7, in good agreement with the accepted value of 2.83.[5] Moreover the ORD and CD curves we obtain from this partially photoresolved complex agree with the published ones.[5,6]

Photoresolution rate curves for *cis*-dioxalatodiaquochromate and the dimer form, di-μ-hydroxy-tetraoxalatodichromate, are shown in Figures 2 and 3. These curves are quite similar to those of Figure 1, for similar reasons. However, in both cases an additional photoreaction must be included: *cis–trans* isomerization in the first case and isomerization between *meso* and enantiomeric forms in the second. ORD–CD curves very similar to that for the tris complex were obtained for these compounds. Because of the additional complexity of the kinetics, rate constants and the value of the dissymmetry factor have not been determined yet. We report also the interesting case of photolytically induced optical activity in the *trans*-dioxalatodiaquochromate isomer, also in Figure 3. Presumably this occurs through photoconversion to the *cis* isomer which then photoresolves, but our data indicate that this does not proceed to the same equilibrium as that obtained when starting with the same concentration of pure *cis* complex.

Acknowledgment. This work has been supported, in part, by grants from the Petroleum Research Foundation and the Rackham School of Graduate Studies at University of Michigan. We also thank C. G. Overberger for the use of a Jasco ORD-UV-5 instrument for the optical activity determinations.

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

(6) J. P. Mathieu, *J. Chim. Phys.*, 33, 87 (1936).

Kenneth L. Stevenson, James F. Verdieck
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

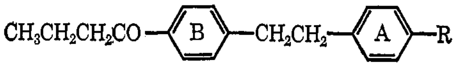
Received February 9, 1968

Charge Migration in Molecular and Fragment Ions

Sir:

Recent investigations[1,2] have produced considerable evidence for the notion[3] that the unimolecular decomposition of ions in a mass spectrometer requires the presence of a positive charge at the site of fragmentation. This has led to the concept of "charge localization" at the point of lowest ionization potential in the molecular ion where it then triggers fragmentation.

One of the most recent examples designed to prove this concept involves various substituted 1-(4-butyrophenyl)-2-phenylethanes (Ia–c).[1b]



Ia, R = NO_2
b, R = NH_2
c, R = $CH_3CH_2CH_2CO$

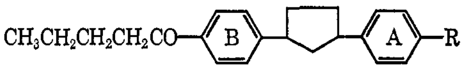
Indeed Ia exhibits intense peaks due to loss of ethylene ("McLafferty rearrangement") or propyl (acyl cleavage) from the substituent on ring B while these are almost completely absent in the spectrum of Ib because the positive charge is thought to reside in ring B of the molecular ion of Ia, but in ring A of that of Ib. The diketone Ic does undergo both reactions, but only once, either at ring A or at ring B.

These authors[1b] consider the possibility that ionization occurs initially at any point of the molecule and it is assumed that the charge migrates rapidly to the site of lowest ionization potential where it then causes fragmentation.

The failure of Ic to undergo fragmentation at the second ketone moiety after initial decomposition of the first is cited[4,5] as evidence for charge localization in the resulting fragment ion.

We felt that this assumption of such a fixation of charge in fragment ions may be unwarranted and the situation may more closely resemble a dynamic distribution of charge which, over a period required for electron impact induced fragmentation ($<10^{-5}$ sec), is statistically maximized at the site of lowest ionization potential (*i.e.*, that the average relative charge density decreases with increasing relative ionization potential of the site).

To test this concept, the mass spectra of a series of compounds (IIa–e),[6] which eliminate the following shortcomings of the diphenylethanes (Ia–c) in this respect, were taken: (1) the absence of the C_2 bridge eliminates the undesirable competing benzyl bond cleavage (which consumes most of the molecular ions of Ib); (2) the McLafferty rearrangement of the valeryl group involves the elimination of propylene rather than ethylene, the loss of which is well known[8] to be much less favorable; and (3) the use of an N-acyl group (which by elimination of ketene results in the equivalent of the molecular ion of the corresponding amine) provides positive proof[9] that the charge is at least at one time concentrated on ring A.



IIa, R = NO_2
b, R = NH_2
c, R = $CH_3(CH_2)_3CO$
d, R = $NHCOC_2H_5$
e, R = $N(COC_2H_5)_2$

---

(1) (a) F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967); (b) T. Wachs and F. W. McLafferty, *ibid.*, **89**, 5044 (1967).

(2) H. Bruderer, W. Richter, and W. Vetter, *Helv. Chim. Acta*, **50**, 1917 (1967).

(3) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93; J. S. Shannon, *Tetrahedron Letters*, 801 (1963); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 9.

(4) Reference 1b, footnote 12.

(5) Formation of secondary ions which involves reaction at the second ketone moiety of Ic after initial decomposition of the first was thought to be so impossible that the low-intensity ions due to $M - C_2H_4 - C_2H_4$, $M - C_2H_4 - C_3H_7$, and $M - C_2H_4 - C_4H_9O$ in the spectrum of Ic were suggested to involve at least in part loss of C_2H_4 from the center of the molecule.[4]

(6) Prepared from 1,3-diphenylcyclopentane:[7] IIc by acylation and IIa by partial nitration followed by acylation; IIb by reduction of IIc. Acylation of IIb with boiling propionic anhydride gave IIe, while cold anhydride in pyridine yielded IId. The spectral properties (uv, ir, nmr, and mass spectra) confirm the structures shown. The stereochemistry is not yet established and will be discussed in the full paper.

(7) S. Eskola, *Ann. Acad. Sci. Fennicae, Ser. A, II, Chem.*, No. 18 (1946). (The crude product was hydrogenated to remove unsaturated by-products).

(8) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).

(9) Assuming that charge localization is indeed a requirement for fragmentation and that it holds for the elimination of ketene just as well as for the McLafferty rearrangement,[1] acyl cleavage,[1b] and the elimination of water and acids.[2]