leaving only a small concentration in the vapour phase. These findings reflect an interaction between test substances and liquid compounds of low polarity. The introduction of substituents on the benzene ring such as CH_3O (6), NO_2 (7), and Br (16) changed the pattern by exhibiting a somewhat larger absorption of acetone. Benzene derivatives with substituent groups such as NH_2 (1), CHO+OH (3) and Br (16) gave rise to partition spectra exhibiting a lower absorption of benzene compared with the other derivatives of benzene.

Alcohols showed partition spectra characterized by a relatively large absorption of methanol compared with that of acetone (2, 13, 15, 19). A similar pattern was also shown by propionic acid (11), menthone (5), and cyclohexanone (14). A very high absorption of methanol was observed with dimethyl sulphoxide (10) and dimethyl formamide (21). Obviously, a common feature of these cases is an interaction of the polar hydroxyl group of methanol with polar groups of the liquid compound.

A number of compounds such as limonene (4), acetylacetone (8), hexadecane (17), and methyl octanoate (20) showed partition spectra of a type rather similar to that observed with ethylbenzene (9) and mesitylene (18).

Tetranitromethane (12) gave rise to a very characteristic partition spectrum exhibiting a highly selective absorption of tetrahydrofuran. This finding is consistent with the formation of an electron-donor-acceptor complex between tetrahydrofuran and tetranitromethane.

The influence of the temperature on the partition spectra was also studied for some of the organic liquids of this series. As expected, the deviation from the 4×25 per cent composition of the test vapour was found to increase at lower temperatures, and decrease at higher ones, as compared with the results obtained at $+20°C$.

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Optical Activity Developed by Preferential Racemization of One Enantiomer in Racemic Cr(III) (ox)₃³⁻ Induced by Irradiation with Circularly Polarized Light

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The idea of using *circularly polarized light* in photolysis to produce optical activity is not new. In 1925 Zocher and Coper [1] reported that on exposing a colloidal silver halide, they obtained a "circular double refractive" colloid of silver. In 1929 Kuhn [2] showed that a partial activation could be obtained by photodecomposition of racemic 2-bromopropanoic acid ethylester with circularly polarized light. A few similar experiments were performed at about the same time.[3-5] The reaction mechanism was not investigated, however, in any of these studies, and especially in the last mentioned case,[5] in which "an asymmetric catalysis" is proposed to take place in a mixture containing only *non*-dissymmetric species, the effect seems dubious.

In this laboratory a generator for circularly polarized light has been built, and a series of photolyses using this type of light have been performed on oxalates of iron(III), cobalt(III), and chromium(III) and on diamine complexes of cobalt(III).[6] The intention of the experiments has been to find a photodecomposition which could be studied at a wavelength where the actual compound has a high circular dichroism (and a low absorption) giving higher light-absorption for circularly polarized light for one of the two diastereomers in a racemic mixture. For several reasons reactions involving a net change (decomposition, ligand exchange, *etc.*) are not very suitable for this purpose. One reason is that the resolution yield reaches its maximum at a conversion of about 50 % and then decreases. Another reason is the change in absorbance due to the decrease in concentration of the reacting species or to a high absorptivity of the product. Thus it was found when repeating the experiment of Kuhn in this laboratory, that the absorbance (270—300 nm) first decreased indicating indeed a decomposition of the

2-bromopropanoic acid ethylester but after a few hours of irradiation the absorbance had *increased* by 100 %. This was found in ethanol as well as in a photolytically inert medium, CCl_4, and the observed rotation was only one tenth of that calculated.[6]

An ideal reaction should therefore be a cyclic one regenerating the reactant. Such a reaction is the *photoracemization* $(+)A \rightarrow (\pm)A$ or $(-)A \rightarrow (\pm)A$ *used on a racemate*. This is the preliminary report of a *photoresolution* of chromium(III) oxalate, $Cr(ox)_3{}^{3-}$, by using its ability to photoracemize[7] and to display no other photochemical reaction, such as photoreduction or the like.

Potassium trioxalatochromate(III), $K_3Cr(C_2O_4)_3 \cdot H_2O$ was prepared in the usual way.[8] The absorptivities of the two maxima in the visible range ($\varepsilon_{432} = 97$ M^{-1} cm^{-1}, $\varepsilon_{571} = 74$ M^{-1} cm^{-1}) agreed perfectly with the value reported by McCaffery, Mason and Ballard.[9] The $A_1 \rightarrow E_a$ transition component of the 571 nm band cannot be observed separate from the $A_1 \rightarrow A_2$ transition in the solution absorption spectrum, but it gives rise to a *circular dichroism* band at 552 nm,[9] which has a very high dissymmetry factor,[10] $g = \Delta\varepsilon/\varepsilon$ ($\Delta\varepsilon_{552}$ of $(+)Cr(ox)_3{}^{3-}$ is 2.83 M^{-1} cm^{-1} and with $\varepsilon_{571} = 74$ M^{-1} cm^{-1} one obtains $g = 0.04$). By using a filter to

Fig. 1. Racemization of a 3.0 mM $(+)Cr(ox)_3$ (strychnine)$_3$ solution in 60 % methanol. To some extent methanol depresses the spontaneous racemization.[7] Upper line: sample in darkness, *i.e.*, spontaneous racemization. Lower line: photoracemization.

exclude light with wavelengths shorter than 500 nm and a super highpressure mercury lamp (described elsewhere[12]) giving an emission maximum at 550 nm, it is possible to concentrate the luminous energy on the part of the band having the positive sign in $(+)Cr(ox)_3{}^{3-}$ (*i.e.*, the E_a band).

$(+)Cr(ox)_3(strychnine)_3$ was prepared according to a method of Mathieu[11] from $K_3Cr(ox)_3$ and strychnine nitrate. Fig. 1 shows the result of a photolysis of $(+)Cr(ox)_3{}^{3-} + 3$ strychnine$^+$ using the arrangement above but with the polarizer adjusted to give *plane polarized light* only (*i.e.*, equal amounts of left and right circularly polarized light). The logarithm of the optical rotation, α, has been plotted *versus* the time. The upper curve shows the decay in optical activity of a solution kept in the *dark*. Both the reactions are of *first order* and they have the rate constants (considering the optical activity only) $k_{dark} = 0.45 \times 10^{-2}$ min^{-1} and $k_{phot} = 2.26 \times 10^{-2}$ min^{-1}, given by the slopes of the lines. (The slope of the upper line gives k_{dark} and the slope of the lower line gives $k_{dark} \times k_{phot}$).

The *maximum possible resolution* has been estimated using the limiting equation:[6] $C_+ \times \varepsilon_+ = C_- \times \varepsilon_-$ (C and ε are the concentrations and absorptivities — for circularly polarized light — respectively, of the corresponding enantiomers). The limiting ratio, $C_+/C_- = (2+g)/(2-g) = 1.041$, suggests a maximum concentration difference $|C_+ - C_-| = 0.081$ mM, if starting from a 4.0 mM $Cr(ox)_3{}^{3-}$ solution. This implies a maximum polarimeter reading of 0.0084°, as the path length of the cell used was 1.50 cm and the specific rotation of $(+)K_3Cr(ox)_3{}^{3-}$ was $[\alpha] = +1600°$ at the actual wavelength (589 nm).[8]

A 4.00 mM racemic $K_3Cr(ox)_3$ solution in 60 % methanol was exposed to *circularly polarized* light from the light source used in the racemization experiment. After only 10 min a small activity could be detected. The sign of the rotation was positive with right circular polarization and negative with left circular polarization. This was expected, as the $(+)$ $Cr(ox)_3{}^{3-}$ exhibits positive circular dichroism in the E_a band,[9] and should therefore have a higher absorptivity to left circular polarized light than $(-)Cr(ox)_3{}^{3-}$ (and *vice versa*). As is shown clearly in Fig. 2, the optical rotation reaches a maximum equilibrium value, $\alpha_{max} = 0.005°$. As a matter of fact a value lower than 0.008° is indeed to be expected as, of course, the *dark racemization* will occur also here. A rough estimate of the effect of the dark racemization is obtained with the decrease in optical activity expected for a separate solution after 100 minutes (*cf.* Fig. 2): $\log(0.008/\alpha_{100}) = 100 \times 0.45 \times 10^{-2}/\ln 10$, $\alpha = 0.005°$.

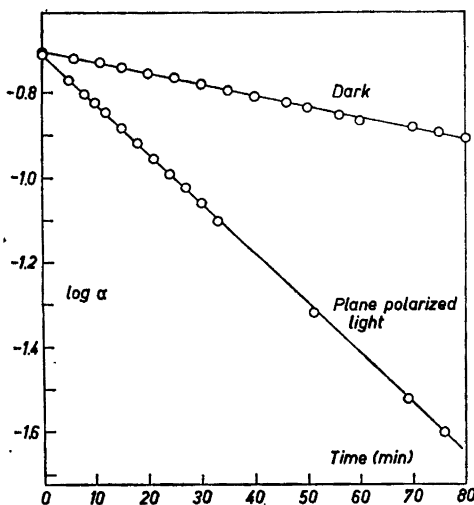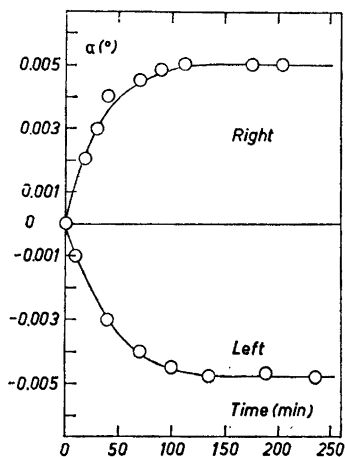Fig. 2. Two photolyses of a 4.00 mM racemic $Cr(ox)_3^{3-}$ solution in 60% methanol, one with *right* and one with *left circularly polarized* light. The same light intensity is used as in the earlier racemization (Fig. 1).

The experiments have been performed at 25.5°. The optical rotation was measured with a modified (see Ref. 6) Perkin Elmer Polarimeter 141. The stop-watch was stopped (for about 30 sec) during the measurement. No decomposition reaction could be detected as the absorption curves (measured with a Hitachi EPS – 3T spectrophotometer) were found to be identical (maximum change 0.5 %) before and after irradiation.

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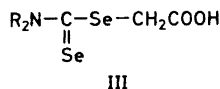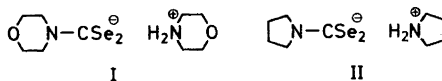
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Organic Selenium Compounds

VII. Preparation of Some Derivatives of Diselenocarbamic Acid

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In connection with studies of the infrared [1] and electronic [2] spectra of organic sulfur and selenium compounds, as well as with studies of coordination compounds with seleniumcontaining ligands,[3] we have prepared several diselenocarbamates and their carboxymethyl esters (or [(N,N-dialkylselenocarbamoyl)seleno] acetic acids). Most of the diselenocarbamates have previously been described by Barnard and Woodbridge,[4] and Rosenbaum et al.[5] but two new diselenocarbamates, derived from morpholine and pyrrolidine, respectively, are described in the following. The carboxymethyl esters are new. They were prepared in the same manner as the corresponding carboxymethyl dithiocarbamates.[6]

$$\text{O}\underset{}{\bigcirc}\text{N-CSe}_2^{\ominus} \quad \text{H}_2\overset{\oplus}{\text{N}}\underset{}{\bigcirc}\text{O} \qquad \underset{}{\bigcirc}\text{N-CSe}_2^{\ominus} \quad \text{H}_2\overset{\oplus}{\text{N}}\underset{}{\bigcirc}$$

$$\qquad\qquad \text{I} \qquad\qquad\qquad\qquad \text{II}$$

$$R_2N-\overset{\underset{\|}{Se}}{C}-Se-CH_2COOH$$

$$\text{III}$$

a: R = C_2H_5

b: R = $\underline{n}-C_3H_7$

c: R_2 = $H_2C\overset{CH_2-CH_2-}{\underset{CH_2-CH_2}{\diagdown}}$

d: R_2 = O$\overset{CH_2-CH_2-}{\underset{CH_2-CH_2}{\diagdown}}$

e: R_2 = $\overset{CH_2-CH_2-}{\underset{CH_2-CH_2}{|}}$

Experimental. Morpholinium morpholine-4-carbodiselenoate (I). A solution of 3.4 g of carbon diselenide, in 50 ml of petroleum ether, was added gradually with stirring, to a cooled

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