[CONTRIBUTION FROM THE INSTITUTE FOR PHYSICAL CHEMISTRY, TECHNISCHE HOCHSCHULE, KARLSRUHE, GERMANY]

The Circular Dichroism of Optically Active β-Octyl Nitrite in the Vapor State

BY HERVEY B. ELKINS[1] AND WERNER KUHN

The optical activity exhibited by the absorption bands of optically active compounds is, as is well known, due to the fact that the electrical vibrations in question possess components oblique to each other in various parts of the molecule.[2] The anisotropic factor is dependent exclusively on the angular and spacial distribution of the electric vibration which corresponds to a given wave length.

$$g = (\kappa_l - \kappa_r)/\kappa \qquad (1)$$

The experimental determination of this factor makes possible a comparison of the vectorial (or tensorial) properties of various absorption bands or of the various parts of one absorption band. In equation (1), κ_l and κ_r are the molecular absorption coefficients for left-hand and right-hand circular polarized light, $\bar{\kappa}$ is the mean value of κ_l and κ_r, equal to the absorption coefficient in unpolarized light. κ is defined as $0.9/cd \log I_0/I$, c being the concentration in moles per liter, d the layer thickness in cm.; 0.9 is the correction factor required when a sector method of absorption measurement is used.

It has been found in previous work,[3] and confirmed by others[4] in numerous cases that the anisotropic factor g as a rule keeps constant throughout a given absorption band, but changes greatly in magnitude, and sometimes even in sign, from one band to another. The conclusion was drawn[3] that the *spacial and angular distribution of the electric vibration of an absorption band was dependent only upon the electronic transition which causes the absorption band, and that it was to practically no extent dependent upon the vibrations or rotations superimposed.* In the few cases where the anisotropic factor underwent large changes in the region of an absorption band, it could be shown that the band was only apparently homogeneous and was in reality composed of two or more overlapping bands, caused by different electronic transitions.[5]

In one apparently simple case, namely, that of β-octyl nitrite, an unexpected behavior was observed.[6] This compound, in common with all alkyl nitrites, has an isolated absorption band between 4000 and 3200 Å. This band is split up into several narrower bands, due to internal molecular vibrations superimposed on the common electronic transition. (Actually there are two different electronic transitions, as measurements of rotation and circular dichroism have shown. Compare the following discussion and Ref. 6.) The anisotropic factor g, in this absorption region, was found to behave very erratically. Instead of being constant, it changed sign or dropped to zero at the various absorption minima. Later measurements by W. Kuhn and H. Biller showed that methylcyclohexyl and methylphenyl nitrites, respectively, exhibited a similarly erratic behavior.[7] *The angular and spacial distribution of the vibrating electric moment thus apparently undergoes a change in each single narrow band, producing a definite value of g in the middle, whereas no optical activity is exhibited at its edges.*

As all previous experiments were made in hexane solution, the influence of the solvent suggested a possible explanation of this phenomenon. In order to avoid any ambiguity in this respect, the present experiments were carried out in the vapor state. It was found that even in the vapor state the absorption spectrum of β-octyl nitrite shows no fine structure but is absolutely continuous, as curve 1 of Fig. 1 shows. It was thought that this might be caused by the magnitude of the molecule, $CH_3CHONOC_6H_{13}$,[8] which with its long side chain is capable of assuming various and great inertial momenta. The absorptions of other nitrites, namely, isoamyl nitrite, $CH_3C_2H_5CHCH_2ONO$,[8] and methyl nitrite,[9] were therefore examined, also in the vapor state, using an underwater spark with aluminum electrodes as a source of continuous

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[1] Sheldon Traveling Fellow from Harvard University.

[2] W. Kuhn and K. Freudenberg, "Hand. u. Jahrbuch d. Chem. Physik," Vol. 8, III (1932); W. Kuhn and K. Bein, *Z. physik. Chem.*, **22B**, 406 (1933).

[3] W. Kuhn and E. Braun, *ibid.*, **8B**, 445 (1930).

[4] *E. g.*, S. Mitchell and S. B. Cormack, *J. Chem. Soc.*, 415 (1932); T. M. Lowry and H. Hudson, *Phil. Trans.*, **232A**, 117 (1933).

[5] W. Kuhn and H. K. Gore, *Z. physik. Chem.*, **12B**, 389 (1931).

[6] W. Kuhn and H. L. Lehmann, *Z. Elektrochem.*, **34**, 549 (1931); *Z. physik. Chem.*, **18B**, 32 (1932).

[7] W. Kuhn and H. Biller, *Z. physik. Chem.*, in press.

[8] Prepared from the carbinol by the method of Beauveault and Wahl, *Compt. rend.*, **136**, 1564 (1903), with modifications suggested by K. Freudenberg and H. Biller.

[9] Prepared by the method of Thiele and Eichwede, *Ann.*, **311**, 366 (1900), and fractionally distilled.

ultraviolet light. The band structure was more distinct than in the case of β-octyl nitrite, particularly in the case of methyl nitrite, but no trace of rotational fine structure could be detected. It is therefore possible, though not probable,[10] that the absence of fine structure in the nitrite absorption bands is due to predissociation.

Curve 2 in Fig. 1 represents the absorption of β-octyl nitrite in hexane as determined by Kuhn and Lehmann; curves 3 and 4, representing amyl and methyl nitrite, are only approximate. It can be stated that the narrow bands[11] of isoamyl nitrite are about 50 Å. nearer the visible than those of methyl nitrite, with the single exception of the band at 3900 Å., which is broader than the other bands and keeps a constant position, or even shifts in the direction of shorter wave lengths in going from methyl to isoamyl nitrite. The shift in direction of longer wave lengths in the main absorption bands, and the shift toward the shorter wave lengths in the band which is nearest the visible, are continued and even more pronounced if isoamyl nitrite is compared with β-octyl nitrite. It is probable that the band at 3720 Å. in amyl nitrite corresponds to that at 3870 Å. in β-octyl nitrite. Furthermore, the measurements of the dichroism of methylphenyl nitrite by Kuhn and Biller indicate that in this compound the corresponding band is at 3960 Å., a shift of over 300 Å. from methyl nitrite; while at the same time the long wave length band at 3900 Å. in methyl nitrite is moved to 3700 Å. in methylphenyl nitrite. *The simultaneous existence of two independent systems of bands in our absorption region will be corroborated by the following investigation of the optical activity.*

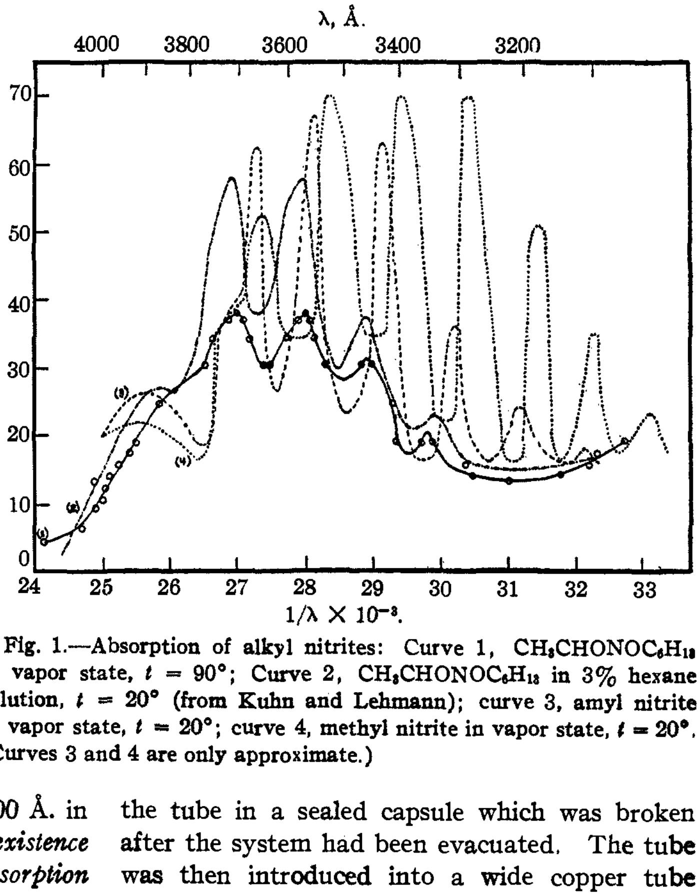

Fig. 1.—Absorption of alkyl nitrites: Curve 1, $CH_3CHONOC_6H_{13}$ in vapor state, $t = 90°$; Curve 2, $CH_3CHONOC_6H_{13}$ in 3% hexane solution, $t = 20°$ (from Kuhn and Lehmann); curve 3, amyl nitrite in vapor state, $t = 20°$; curve 4, methyl nitrite in vapor state, $t = 20°$. (Curves 3 and 4 are only approximate.)

Curve 1 in Fig. 2 shows the circular dichroism $(\kappa_l - \kappa_r)$ of dextro β-octyl nitrite in the vapor state. It is, according to our knowledge, the first measurement of circular dichroism that has been made upon a gas, inasmuch as previous observations have related to liquids exclusively. The measurements were carried out according to the method described by Kuhn and Braun.[3] The substance was contained in a tube of fused silica measuring 4 cm. in diameter and 1 meter in length with plane parallel end-plates.[12] A known quantity of substance (*e. g.*, 0.2 g.) was introduced into the tube in a sealed capsule which was broken after the system had been evacuated. The tube was then introduced into a wide copper tube heated electrically from the outside. It was maintained at a temperature of 90°, which was sufficiently high to ensure the evaporation of all the substance. Octyl nitrite was found to boil at various pressures as follows: 2.2 mm. at 30°; 4.9 mm., 40°; 8.0 mm., 50°; 11.5 mm., 60°; 15 mm. at 65°.[13] Total evaporation of 0.2 g. of the substance in our tube should be obtained at 70–75° according to an extrapolation of these values.

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(10) If the broadening of the absorption bands were due to predissociation, one would expect the long wave end of the system to be less diffuse than the short wave region. This, however, was not the case. We therefore expect that the absence of fine structure in this system is due to another cause, discussed later in this article.

(11) It is interesting to note that in spite of the fact that all these nitrites, as Fig. 1 shows, have similar band structures, previous workers have found only a single band at 3850 to 3000 Å. in the cases of amyl, ethyl and nonyl nitrites. *Cf.* Baly and Desch, *J. Chem. Soc.*, **93**, 1747 (1908); Harper and Macbeth, *ibid.*, **107**, 87 (1915); Pickard and Hunter, *ibid.*, **123**, 434 (1923). It is possible that this failure to resolve the band was due to inadequate apparatus, or to the fact that polar solvents (ethyl alcohol and, in the case of nonyl nitrite, the pure substance) were used.

(12) A slight double refraction of the end-plates, resulting in a shift of the zero point in the measurement of dichroism, necessitated a correction throughout the experiments.

(13) This last point is taken from Beilstein.

In these measurements of circular dichroism both the levo- and dextro-rotatory compounds were used. The values obtained with the antipodes were of the same magnitude, but of opposite sign. The data given in Fig. 2 contain the measurements carried out with both antipodes, the sign corresponding to the dextro-rotatory nitrite. The optically active forms of β-octyl nitrite were prepared by the usual method[8] from the active isomers of the carbinol, which were prepared from the racemic carbinol (Kahlbaum) by the method described by Pickard and Kenyon.[14] The active carbinols had specific rotations of +9.92 and −9.48°, respectively. Pickard and Kenyon give a value of ±9.92° for the completely resolved carbinol. The nitrites prepared from these carbinols gave specific rotations of approximately −5.45 and +4.5°, whereas Lehmann gave +5.56° for the pure nitrite prepared from the dextro carbinol. The values plotted in Fig. 2 correspond to 100% active material.

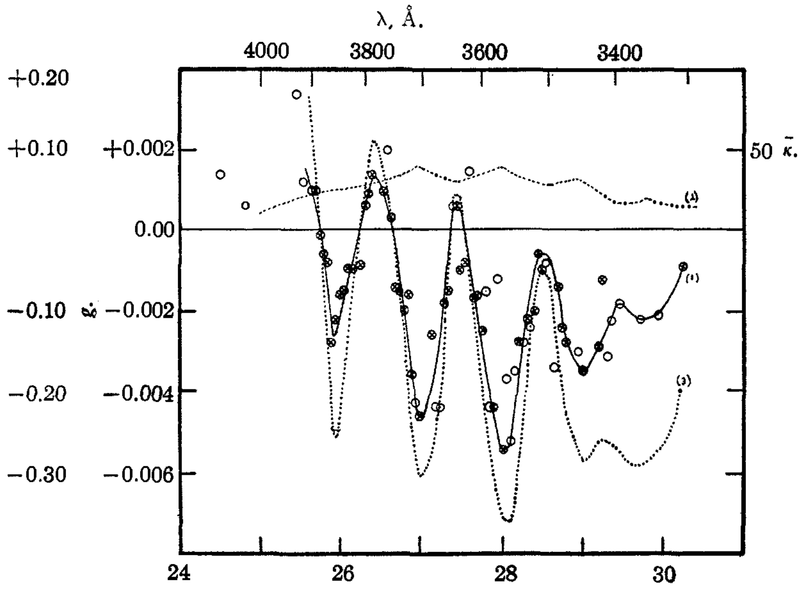

Fig. 2.—Curve 1, circular dichroism of $CH_3CHONOC_6H_{13}$ in vapor state, $t = 90°$ (crossed circles represent averages of two or more concordant results); curve 2, absorption of $CH_3CHONOC_6H_{13}$ in vapor state, $t = 90°$; curve 3, anisotropic factor of $CH_3CHONOC_6H_{13}$ in vapor state, $t = 90°$.

By combining the observed dichroism with the absorption according to equation (1), we find the anisotropic factor (curve 3, Fig. 2). If the angular and spacial distribution of the vibrating electric moment were the same throughout the absorption region considered, the anisotropic factor would be a constant. Curve 3 shows that this is not even approximately the case.

The circular dichroism of the vapor as well as its absorption is similar to that in hexane solution. *The change in anisotropic factor observed in solution therefore cannot be due to the influence of the solvent: it must be a property of the molecule itself.* As is shown by the work of Kuhn and Biller, a similar behavior of the anisotropic factor is found in the case of hexane solutions of methylcyclohexyl nitrite and methylphenyl nitrite. It is almost certain that the enormous fluctuations of the anisotropic factor in these cases also reveal a property of the molecule, not an influence of the solvent.

The fact that the circular dichroism, which is predominantly negative in the main absorption region, becomes positive at the long wave length end of the system, was interpreted by Kuhn and Lehmann to mean the existence of a second electronic transition producing a weak absorption in this spectral region. This explanation will certainly hold for the vapor as well.

This conclusion is supported by an examination of the absorption spectra. In β-octyl nitrite as well as in isoamyl and methyl nitrites the absorption spectrum consists primarily of a main system of distinct small bands spaced at nearly equal intervals, which will be called system I. A disturbance of this regularity, also found by Kuhn and Biller for methylcyclohexyl nitrite, is observed in the long wave length region in all cases. This confirms the existence of a second weak absorption system, called system II.

It is clear that system II as well as system I is characteristic for the O-N-O group, and it is probable that the two are intimately connected. Quite possibly the two systems of bands correspond to one degenerate system in the case of the O-N-O radical, and this may be split up into

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(14) Pickard and Kenyon, *J. Chem. Soc.*, **91**, 2058 (1907); **99**, 45 (1911); **103**, 1923 (1913).

two independent absorption systems with neighboring frequencies by the disturbing influence of the alkyl groups present in the nitrites.[15]

While it is certain that the existence of system II explains the behavior not only of the absorption but also of the circular dichroism in the *long wave length* portion of the absorption region, it is not clear whether the fluctuations of the anisotropic factor at shorter wave lengths, *e. g.*, around 3500 Å., are wholly or in part to be similarly explained. It is quite possible to represent the observed absorption as the sum of the absorption coefficients belonging to systems I and II, respectively

$$\kappa = \kappa_{I} + \kappa_{II} \qquad (2)$$

and similarly to represent the observed circular dichroism

$$\kappa_{l} - \kappa_{r} = g_{I}\kappa_{I} + g_{II}\kappa_{II} \qquad (3)$$

g_{I} and g_{II}, the anisotropic factors for systems I and II, are negative and positive, respectively. It is clear from an examination of curves 1 or 3, Fig. 2, that at 3900 Å. and at 3770 Å. the numerical value of $g_{II}\kappa_{II}$ exceeds that of $g_{I}\kappa_{I}$, while at 3850 Å. the reverse is true. We can go farther, assume that g_{I} and g_{II} are constant, and assign to each a definite value. By combining equations (2) and (3), hypothetical absorption curves for system I and for system II may then be calculated from the observed absorption and circular dichroism. Such an hypothesis avoids the necessity of postulating an absorption system with an inconstant anisotropic factor; but it requires that system II extend to 3450 Å. or farther in the ultraviolet. While there is no evidence of such an extension obtainable from the absorption measurements on β-octyl, methylcyclohexyl, amyl or methyl nitrites, it is possible, though not very probable, that system II may extend beyond the long wave length region.

If the observed fluctuations in anisotropic factor in the mean and short wave length region are not due to the superposition of two optically active systems (I and II), the irregularities must be a property of the single absorption bands of these nitrites. They would in this case be due to the mechanical effects which produce the broadening of the small absorption bands and cause the absence of a rotational fine structure in the absorption spectrum of the vapor.[7] The great alkyl radicals may in fact act as a kind of solvent with respect to the nitrite group; the middle and the edge of a single band would correspond to different constellations and therefore to different mechanical actions exhibited by the rest of the molecule on the chromophoric group (O-N-O). The difference in anisotropic factor observed would mean that these different mechanical actions also produce different spacial and angular distributions of the vibrating electric moment. Especially the components of the vibration which are induced in the neighboring substituents by coupling forces and which possess the frequency of the nitrite group vibration can, from a theoretical standpoint, be expected to depend in a sensitive way on the constellation of these substituents; and we know that there are just these sensitive components which play the decisive part in optical activity.

It is hoped that projected measurements at low temperatures may throw further light on these questions.

Summary

1. The ultraviolet absorption spectra of gaseous methyl, isoamyl and β-octyl nitrites were examined and compared. No fine structure was observed in any case, but the individual bands were sharper and shifted toward the ultraviolet in the simpler and smaller molecules.

2. The first known measurements of the circular dichroism of a gas were made upon the vapor of β-octyl nitrite at 90°. The great inconstancy of the anisotropic factor, previously observed in hexane solutions of this and other alkyl nitrites but in no other cases, was found to be a property of the vapor state as well.

3. The anomaly was thus shown to be a property of the alkyl nitrite molecules themselves, and not a solvent effect. It is at least partly due to the fact that the absorption in the region considered (3900 to 3100 Å.) has to be attributed to two different electronic transitions producing an anisotropy of opposite sign and showing a shift in wave number of opposite sign if the various nitrites are compared.

It is probable that the overlapping of two absorption systems explains only part of the behavior of the anisotropic factor and that the rest of the fluctuations observed, as well as the absence of rotational fine structure in the absorption spectra, are due to mechanical effects exhibited by the rest of the molecule on the chromophoric group.

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(15) Compare W. Kuhn and K. Bein, *Z. anorg. allgem. Chem.*, **216**, 321 (1934); *Z. physik. Chem.*, **24B**, 335 (and especially p. 340) (1934), where an example of this kind is treated theoretically in the case of organic and inorganic asymmetric compounds.