

somewhat similar results have been reported for some other reactions.⁷ (The high value of $N_{\text{Ald}}^0/N_{\text{Alc}}^0$ cannot be attributed to tritium enrichment of the aldehyde by further oxidation, since the amount of benzoic acid formed in the early stages of the oxidation is too small to affect the results significantly.)

There is a possible alternative explanation for a value of $N_{\text{Ald}}^0/N_{\text{Alc}}^0$ greater than one-half which does not require that k_3/k_1 be greater than unity. If some process occurred without C—H bond rupture in the rate-determining step, there would be little or no difference in reaction rate between PhCH_2OH and PhCHTOH , but there might still be a large intramolecular isotope effect ($k_{\text{T}}/k_{\text{H}}$) for a molecule of PhCHTOH in a subsequent fast step. For such a process, $N_{\text{Ald}}^0/N_{\text{Alc}}^0$ would be equal to $1/(1+k_{\text{T}}/k_{\text{H}})$ with a value between 0.5 and 1. If 23% of the alcohol were oxidized by a process with no intermolecular isotope effect and an intramolecular isotope effect, $k_{\text{T}}/k_{\text{H}}$, of 0.19, and the balance of the alcohol were oxidized by a process with an intermolecular isotope effect k_2/k_1 and an intramolecular isotope effect k_2/k_3 both equal to 0.19, the calculated values of " $k_{\text{PhCHTOH}}/k_{\text{PhCH}_2\text{OH}}$ " and of $N_{\text{Ald}}^0/N_{\text{Alc}}^0$ would be 0.69 and 0.58, respectively, as observed.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 125th meeting of the American Chemical Society, Kansas City, Missouri, April, 1954.

† Present address: Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma.

¹ F. H. Westheimer and N. Nicolaidis, *J. Am. Chem. Soc.* **71**, 25 (1949).

² L. Kaplan, *J. Am. Chem. Soc.* **77**, 5469 (1955).

³ F. H. Westheimer, *Chem. Revs.* **45**, 419 (1949) and later papers.

⁴ Wilzbach, Kaplan, and Brown, *Science* **118**, 522 (1953).

⁵ L. Kaplan, *J. Am. Chem. Soc.* **76**, 4645 (1954).

⁶ J. Bigeleisen, *Science* **110**, 14 (1949).

⁷ D. W. Coillet and G. M. Harris, *J. Am. Chem. Soc.* **75**, 1486 (1953); G. M. Harris, *J. Phys. Chem.* **56**, 891 (1952).

Note on the Infrared Dichroism of Axially Oriented Polymers

S. KRIMM

Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan

(Received August 24, 1959)

IT has been pointed out¹ that, in cases where it is permissible² to consider a polymer as being constituted of a fraction f of chains aligned exactly parallel to the fiber axis, the remainder, $1-f$, being completely randomly oriented, it is possible to place significant limits on the angle θ which a transition moment makes with the molecular chain axis. This does not depend upon prior knowledge of f or of $R_0=2 \cot^2\theta$, the dichroic ratio of a perfectly aligned set of chains. It may be of

interest to note that in certain special cases, which are, however, of frequent occurrence in polymers, the angle θ can be uniquely determined, and therefore also the quantity f . This occurs under certain circumstances when two transition moments associated with a portion of the molecule are perpendicular to each other, such as those of $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$, and the amide I and amide V bands of the peptide group.³

Suppose that two transition moments \mathbf{M}_1 and \mathbf{M}_2 are perpendicular to each other, \mathbf{M}_1 making an angle of θ_1 with the molecular chain axis. If \mathbf{M}_2 makes an angle ω with the plane defined by \mathbf{M}_1 and the chain axis, then the angle between \mathbf{M}_2 and the chain axis is given by $\cos\theta_2 = \cos\omega \sin\theta_1$. Thus, if

$$R_{01} = 2 \cot^2\theta_1, \quad (1)$$

then

$$R_{02} = 4 \cos^2\omega / (R_{01} + 2 \sin^2\omega). \quad (2)$$

By using the relationship⁴

$$f = [(R-1)(R_0+2)] / [(R_0-1)(R+2)], \quad (3)$$

where R is the observed dichroic ratio, and equating the right hand side of Eq. (3) for the two bands, we find that

$$\cot^2\theta_1 = \{[A - B(1 - 3 \cos^2\omega)] / 2A + B\}, \quad (4)$$

where

$$A = (R_1 + 2)(R_2 - 1),$$

$$B = (R_2 + 2)(R_1 - 1). \quad (5)$$

Since A and B are experimentally determined quantities, θ_1 can be obtained if ω is known (except for the case $\omega = \pi/4$).

Two interesting special cases of Eq. (4) are often found in polymers, viz., $\omega = 0$ and $\omega = \pi/2$. These correspond to \mathbf{M}_2 being in the plane formed by \mathbf{M}_1 and the chain axis direction, and \mathbf{M}_2 perpendicular to this plane, respectively. For these cases

$$\cot^2\theta_1 = (A + 2B) / (2A + B), \quad \text{for } \omega = 0, \quad (6)$$

$$\cot^2\theta_1 = (A - B) / (2A + B), \quad \text{for } \omega = \pi/2. \quad (7)$$

Thus, no assumptions as to the chain orientation distribution or fraction of disordered material are required. In fact, after θ_1 is determined f can be found from Eq. (3), and using this f the θ values for other modes can immediately be obtained from the observed dichroic ratios of their bands. It is pertinent to note that observations on three mutually perpendicular moments will not permit determination of ω in general, since in this case R_{03} is not independent of R_{01} and R_{02} .

¹ R. D. B. Fraser, *J. Chem. Phys.* **29**, 1428 (1958).

² M. Beer, *Proc. Roy. Soc. (London)* **A236**, 136 (1956).

³ Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.* **24**, 408 (1956).

⁴ R. D. B. Fraser, *J. Chem. Phys.* **24**, 89 (1956).