available instrumentation) alone is too weak and ill-resolved to permit positive conclusions. The strong *a* and *b* branches of the C=O stretching band around 1700 cm.$^{-1}$ show that the carboxyl groups are again tilted in this projection. The hydrocarbon chains must be considerably twisted—probably because of relatively strong interactions between the π orbitals of the double bonds—to account for these observations.

The 1190–1352 cm.$^{-1}$ region of the spectrum deserves a few remarks. The carboxyl deformation band usually found in this region cannot be distinguished from the series of five equally spaced relatively strong bands, which are related to the chain length between the carboxyl group and the double bond.[31] The five bands have components along all three axes and therefore probably do not arise in a simple manner from parallel or perpendicular modes of isolated chains. The four much weaker bands between 1352 and 1313 cm.$^{-1}$, on the other hand, are polarized essentially along the *c*-axis, which is compatible with a CH_2 wagging assignment.

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PHILADELPHIA, PA.

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The Optical Rotation of Oriented Helices. I. Electrical Orientation of Poly-γ-benzyl-L-glutamate in Ethylene Dichloride

BY IGNACIO TINOCO, JR.

RECEIVED JUNE 2, 1958

The change of optical activity in an electric field of poly-γ-benzyl-L-glutamate in ethylene dichloride has been measured as a function of wave length. The difference in specific optical activity parallel and perpendicular to the helical axis $[\alpha_{33}] - [\alpha_{11}]$ varies from about +400 at λ 550 mμ to +1300 at λ 340 mμ. This dispersion follows a one term Drude equation. Comparison of these data with the average rotatory dispersion shows that $[\alpha_{33}]$ is large and positive, while $[\alpha_{11}]$ is large and negative.

Introduction

Much theoretical and experimental work has been done on the optical activity of helical molecules.[1-11] This work has been concerned with the average optical rotation of the molecules. A new method which provides information about the optical activity along specific directions in the molecule has been developed recently.[12,13] This technique, which involves partial orientation of the molecules by an electric field, is described in the present report.

Poly-γ-benzyl-L-glutamate exists as a helix in ethylene dichloride[14,15]; its rotatory dispersion has been studied extensively in this and other solvents.[1,6] Furthermore, PBG helices containing both D- and L- units have been investigated to determine the special contribution of the helix to the average optical activity.[2] We have used PBLG in the present study because it is appreciably oriented in practical electric fields[16] and because of the previous thorough optical activity studies. The main quantity obtained is $[\alpha_{33}] - [\alpha_{11}]$, the difference in the specific optical activity for light travelling parallel and perpendicular to the helical axis. The average optical activity, as commonly measured for molecules in solution, is given by $([\alpha_{33}] + 2[\alpha_{11}])/3$.

Material

A sample of PBLG (No. ES-508) with a weight average molecular weight of 64,000 was very kindly supplied by Dr. E. R. Blout. The sample formed a turbid, conducting solution when dissolved in ethylene dichloride (EDC), therefore it was purified by precipitation prior to use. Acetone, absolute ethanol and petroleum ether were all tried as precipitating agents. Petroleum ether was the best precipitant, but the redissolved PBLG was too conducting. Absolute ethanol finally was chosen as the best agent for precipitating most of the PBLG yet leaving the ionic impurities in solution.

The 1,2-dichloroethane (EDC) was obtained from Eastman Kodak Co. It was refluxed over P_2O_5, distilled and stored in a P_2O_5-containing desiccator. One disadvantage to EDC as a solvent is that PBLG slowly aggregates in it. A fairly concentrated solution of PBLG in EDC became solid after a few months. This gel would not dissolve in more EDC, but it did dissolve in dimethylformamide.

The concentration of solutions were determined by drying the solution overnight at 50° in a vacuum oven.

Methods

Optical Activity.—The change of optical rotation of a solution in an external electric field is measured by applying a field to the transparent electrodes of a cell in a polarimeter. The change of intensity caused by the rotation of the plane of polarization is determined by a photomultiplier and recorder.

The apparatus consists of a Rudolph High Precision Polarimeter with a Beckman DU Spectrophotometer used as a monochromator. As slit widths of 1–2 mm. were used the effective band width was about 10 mμ or more. The light

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(1) J. T. Yang and P. Doty, THIS JOURNAL, **79**, 761 (1957).

(2) P. Doty and R. D. Lundberg, *Proc. Natl. Acad. Sci.*, **43**, 213 (1957).

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(5) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

(6) W. Moffitt and J. T. Yang, *Proc. Natl. Acad. Sci.*, **42**, 596 (1956).

(7) W. Moffitt, *ibid.*, **42**, 736 (1956).

(8) W. Moffitt, D. D. Fitts and J. G. Kirkwood, *ibid.*, **43**, 723 (1957).

(9) D. D. Fitts and J. G. Kirkwood, *ibid.*, **42**, 33 (1956).

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(11) E. R. Blout and R. H. Karlson, THIS JOURNAL, **80**, 1259 (1958).

(12) I. Tinoco, Jr., and W. G. Hammerle, *J. Phys. Chem.*, **60**, 1619 (1956).

(13) I. Tinoco, Jr., THIS JOURNAL, **79**, 4248 (1957).

(14) P. Doty, J. H. Bradbury and A. M. Holtzer, *ibid.*, **78**, 947 (1956).

(15) P. Doty and J. T. Yang, *ibid.*, **78**, 498 (1956).

(16) I. Tinoco, Jr., *ibid.*, **79**, 4336 (1957).

source is a 6 v., 50 c.p. tungsten lamp. An RCA 1P28 photomultiplier tube is the detector; the voltage it develops across a 1M resistor is measured by a Sanborn 151 Recorder.[17]

The usual optical property measured in an electric field is the refractive index. Plane polarized light passing through a solution with an electric field perpendicular to the direction of propagation becomes elliptically polarized because of the different refractive indices produced parallel and perpendicular to the electric field. This phenomenon is known as the Kerr effect.[18] As the change in rotation of the plane of polarization would be difficult to separate experimentally from the Kerr effect, a different method of measurement must be used. Light is therefore passed through the solution parallel to the external electric field. The refractive index change in the field now does not produce any disturbing effects and the rotation can be measured.

The cell is a 3.7 × 3.7 × 2.5 cm. block of Teflon with Corning[19] conducting glass (EC No. 7740) windows 2.3 cm. in diameter. This Corning glass has a resistance of 10 ohm/square and a transmittance of 55% in the visible wave length region. The glass is sealed to the Teflon by the pressure of brass rings threaded into the Teflon. Electrical connection to the inner conducting coating is made through 1 mil platinum rings connected by platinum wires to brass binding posts on the outside of the cell. The platinum rings circle the field of view to help provide a uniform electric field parallel to the direction of the incident light. The glass electrodes are 1.008 cm. apart. The cell, which is filled by a syringe through a small hole in the Teflon block, has a 2 ml. volume. It is held in the light path by a hollow copper container through which water from a 20° thermostat flows. As the room temperature was about 24–25°, the actual temperature in the cell was probably about 22°. The electric field is provided by a regulated 0–10,000 volt d.c. power supply. The voltage was measured with a 2% accuracy by a Weston microammeter in series with a 10.3M resistance. The microammeter was calibrated with a potentiometer.

After various trials the technique given was used for each measurement. At each wave length the optical rotation was first measured in the usual manner by finding positions of equal light intensity on each side of the minimum. The wave length range (340 to 550 mμ) was limited on the ultraviolet side by the absence of quartz optics on the polarimeter and by the presence of the conducting glass windows in the cell. The high wave length side was not extended because the effects in the electric field became very small in this region. The angle which maximized the signal to noise ratio for the measurement then was determined. From the equation for the intensity I as a function of angle θ between analyzer and polarizer

$$I = I_0 \sin^2 \theta + I_s \qquad (1)$$

where I_s is the stray light obtained with crossed nicols, we see that the maximum change in intensity with angle occurs at 45°. However, because of the noise characteristics of the photomultiplier, the optimum angle is not 45° but is given by an equation derived by O'Konski.[20] The optimum angles

$$\sin \theta_{\text{opt.}} \cong \left(\frac{I_s}{I_0}\right)^{1/4} \qquad (2)$$

calculated from this equation was about 10° for the present apparatus. With the analyzer fixed at the optimum angle on one side of the minimum, the electric pulse was applied for a second or less, and the change in light intensity ($I_E - I_0$) was recorded. Then with the field off, the light intensity was calibrated against angle by moving the analyzer to 3 new angles and recording the intensity. By interpolation the change in optical rotation ($\theta_E - \theta_0$) could be obtained. The same procedure then was followed with the analyzer set at the optimum angle on the other side of the minimum. The procedure is best illustrated by Fig. 1. We notice, for example, that if the optical activity increases in an electric field, there will be a decrease in intensity with the analyzer set at +10°. The intensity change due to any other optical phenomenon such as absorption or scattering will be independent of position of the analyzer and can thus be separated.

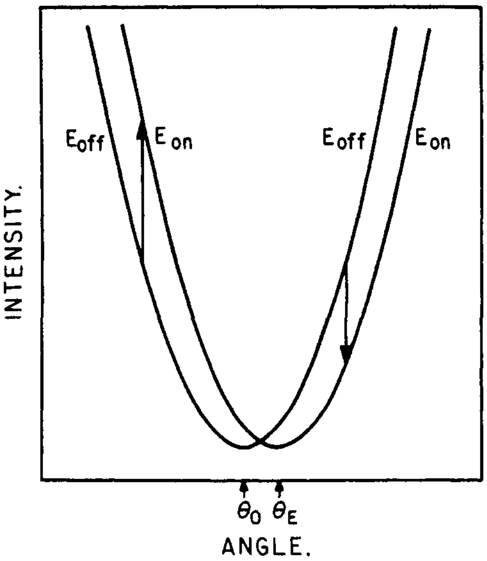

Fig. 1.—An illustration of light intensity *vs.* analyzer angle in a polarimeter. The sign and magnitude of the change of optical rotation in an electric field can be determined from the change of intensity.

Preliminary measurements[18] not reported here were made with other polarimeters. First, a visual, split field polarizer type polarimeter was used. Then, an automatic Rudolph Polarimeter,[21] with a Servo system to find the intensity minimum in the presence of the electric field, was used. All three instruments gave qualitatively the same results. In each instrument the cell filled with pure solvent was tested for any apparent effects. None ever was seen.

Before a recorder and a 1 sec. electric pulse were used, a galvanometer as the output detector of the photomultiplier tube and a static electric field were tried. This was unsuccessful because of refractive index gradients produced in the cell by electric heating. An even shorter electric pulse may be desirable as some heating effects are visible with 1 sec. pulses. Electrode polarization phenomena also would be reduced by use of shorter pulses. There was indication of electrode polarization with some of the more conducting solutions. These results are not reported and no systematic study was made. However, great care was taken in drying solvent and polymer with the final solutions.

Electric Birefringence.—Electric birefringence (Kerr effect) measurements also were made. The apparatus[22] has been described previously[23] except for a few minor modifications.[24] Measurements were made at 30°. Both specific Kerr coefficients (B/c) and rotary diffusion coefficients can be obtained from the data. However, only the former will be discussed at this time.

Theory.—The change in optical activity of a solution of helical molecules in an electric field, for light incident parallel to the electric field, can be written as[18]

$$([\alpha]_E - [\alpha]_0)/E^2 = (2/45)([\alpha_{33}] - [\alpha_{11}])f(p,q,c) \qquad (3)$$

$$\lim_{c \to 0} f(p,q,c) = p_3 + q$$

[ ] designates specific optical activity with units of (deg. ml./dm. g.).

$[\alpha]_E$ = optical activity in the presence of the static electric field E

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[17] We wish to thank Dr. Power Sogo for kindly lending us this recorder.

[18] C. G. LeFevre and R. J. W. LeFevre, *Revs. Pure Appl. Chem.*, **5**, 261 (1955).

[19] We wish to thank Dr. E. M. Greist of Corning Glass Works for kindly furnishing this glass.

[20] C. T. O'Konski and B. H. Zimm, *Science*, **111**, 113 (1950).

[21] We wish to thank Prof. J. B. Nielands and Mr. D. P. Sproul of the University of California Biochemistry Virus Laboratory for the use of this instrument.

[22] We wish to thank Prof. C. T. O'Konski for very kindly allowing us to use this equipment.

[23] C. T. O'Konski and A. J. Haltner, THIS JOURNAL, **78**, 3604 (1956).

[24] W. H. Orttung, Ph.D. Thesis, University of California.

$[\alpha]_0$ = optical activity in the absence of the field. It is the optical activity as usually measured: $([\alpha_{33}] + 2[\alpha_{11}])/3$
$[\alpha_{33}]$ = optical activity for light incident parallel to the helical axis
$[\alpha_{11}]$ = optical activity for light incident perpendicular to the helical axis
E = electrical field strength in (e.s.u.volts/cm.)
c = concn. in (g./ml.)
p_3 = $(\mu_3/kT)^2$. The dipole moment μ_3 must be parallel to the helical axis by symmetry
q = $(\alpha_{E,33} - \alpha_{E,11})/kT$. The electrical polarizabilities are $\alpha_{E,33}$ along the helical axis and $\alpha_{E,11}$ perpendicular to this axis

The left-hand side of eq. 3 is the quantity measured. To determine $[\alpha_{33}] - [\alpha_{11}]$ the orientation function $f(p,q,c)$ must be known. It can be obtained from the analogous equation for electric birefringence[16]

$$B/c = \Delta n/c\lambda E^2 = (2\pi/15\, n\rho\lambda)(g)f(p,q,c) \qquad (4)$$

B/c = specific Kerr coefficient in (cm.^{4} volt^{-2} g.$^{-1}$)
Δn = birefringence
λ = wave length of light *in vacuo*
n = refractive index of soln.
ρ = density of solute
g = difference in optical polarizability (per unit volume of particle) parallel and perpendicular to the helical axis[25]

In eq. 4 the left-hand side is again the quantity measured. Therefore by measuring the optical activity and refractive index change produced by an electric field on the same solution, one can obtain the ratio $[\alpha_{33}] - [\alpha_{11}]/(g)$. As (g) is available from independent measurements such as flow birefringence or depolarization of scattered light, the desired parameter $[\alpha_{33}] - [\alpha_{11}]$ also can be obtained. This is a rather involved method so it might be encouraging to know that a simpler one exists. Equation 3 is correct for values of E which are not too high. For saturating electric fields a more complicated relation exists which can be solved graphically for $[\alpha_{33}] - [\alpha_{11}]$. That is, this parameter can be obtained directly from the optical rotation measurements without need for auxiliary data. Values of (g) have been obtained recently[26] by this method from the analogous eq. 4.

Results

The values of $([\alpha]_E - [\alpha]_0)/E^2$ obtained are given in Table I. Various different voltages were applied to each solution and the change in optical rotation was measured. The change was proportional to the square of the voltage; from the slope of plots of $\theta_E - \theta_0$ *vs.* V^2 the parameters in the table were obtained. The numbers in parentheses show how many different values of voltage were used for each solution. An example of the magnitude of the values actually measured is given in Fig. 2 for a 98 g./l. solution at 380 mμ. We notice that 4,000 practical volts produces about 0.60 degree change in the 1 cm. cell. As the change in angle can only be measured to ± 0.02–0.04 degrees because of heating disturbances, the precision of $([\alpha]_E - [\alpha]_0)/E^2$ is approximately ± 10 to 20%.

TABLE I

THE CHANGE OF OPTICAL ACTIVITY IN AN ELECTRIC FIELD OF POLY-γ-BENZYL-L-GLUTAMATE IN ETHYLENE DICHLORIDE

λ (mu)	$\frac{[\alpha]_E - [\alpha]_0}{E^2}$ (deg. cm.^{5}/dm. g. v.^{2}) 98 g./l.	71 g./l.	$[\alpha_{33}] - [\alpha_{11}] \times 10^{-3}$ (deg. cm.^{3}/dm. g.) 98 g./l.	71 g./l.
340	0.44 (4)	0.26 (3)	1.32	1.28
360	.37 (4)	.24 (3)	1.12	1.14
380	.34 (8)	.21 (4)	1.01	1.01
400	.25 (5)	.18 (4)	0.76	0.82
450	.21 (5)	.12 (3)	.64	.57
500	.15 (4)	.11 (3)	.46	.54
550	.12 (3)	.075 (2)	.38	.36

Values of $[\alpha]_0$ obtained were in reasonable agreement with the extensive previous work of Yang, *et al.*[1,6]

Electrical birefringence measurements were made on the same solutions used for the optical activity studies. A tungsten source without monochromater produced an average wave length of 510 mμ. The same procedure of finding the slope of plots of Δn *vs.* E^2 was used. For the 98 g./l. solution a value of $B/c = 0.127$ cm.^{4} (e.s.u. volt)$^{-1}$ g.$^{-1}$ was obtained from measurements at 5 different field strengths from 300–630 practical volt/cm. A value of $B/c = 0.0793$ was obtained for the 71 g./l. solution; 9 field strengths from 300–2,200 volt/cm. were used. Previous measurements on higher molecular weight PBLG samples[16] in the same solvent lead to $B/c \approx 0.04$ for a 64,000 M_w polymer at infinite dilution. This indicates that the values obtained in the present study are reasonable.

Using values[16] of $n = 1.443$, $\rho = 1.32$ g./ml., λ510 mμ and eq. 3, 4, we obtain $([\alpha_{33}] - [\alpha_{11}])/(g)$. A small correction must be made because of the different temperatures used for the two types of measurements. The correction is a factor of (293/303) raised to a power between 1 and 2. The first power corresponds to induced dipole orientation; the second power corresponds to permanent dipole orientation. The correction is at most 7%. The first power of this factor was used, although there is evidence that permanent dipole orientation may be the more important.[26] As room temperature was about 298°K., it was felt that the actual temperatures of the solution in the two types of measurements were more nearly equal than their corresponding thermostat temperatures.

Professor Doty[27] has very kindly supplied a value of $(g) = 4.1 \times 10^{-3}$ for PBLG in EDC obtained from flow birefringence data. Saturation of electrical birefringence measurements[26] lead to a similar value. We can thus calculate $[\alpha_{33}] - [\alpha_{11}]$ with the results given in Table I and Fig. 3. We notice that these values are independent of concentration. This helps justify our writing of eq. 3 and 4 with the concentration dependence in the orientation function and not in the optical factors.

The dispersion of $[\alpha_{33}] - [\alpha_{11}]$ can be fit by a one term Drude equation.

$$[\alpha_{33}] - [\alpha_{11}] = \frac{94.5 \times 10^6}{\lambda^2 - (212)^2} \qquad (5)$$

The line shown in Fig. 3 is a plot of this equation

Discussion

The fact that the optical rotation increases at all wave lengths in the presence of the electric field immediately shows that the optical activity along the helical axis is larger than that perpendicular to this axis. A complete theory of the optical activity of polypeptide helices would allow us to assign the sense of the helix (right or left handed)

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[25] We use g instead of the common $(g_1 - g_2)$ to designate the anisotropy of the polarizability so as to keep our axis designation of 3 for the helical axis and 1 for the transverse axis.

[26] W. H. Orttung and C. T. O'Konski, personal communication.

[27] J. T. Yang and P. Doty, unpublished measurements.

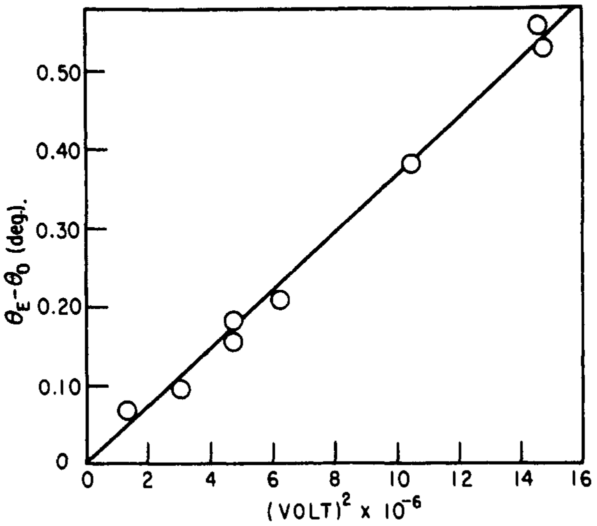

Fig. 2.—The change of optical rotation *vs.* the square of the field (practical volts) for a 98 g./l. solution of poly-γ-benzyl-L-glutamate in ethylene dichloride. The path length is 1 cm. and the wave length is 380 mμ.

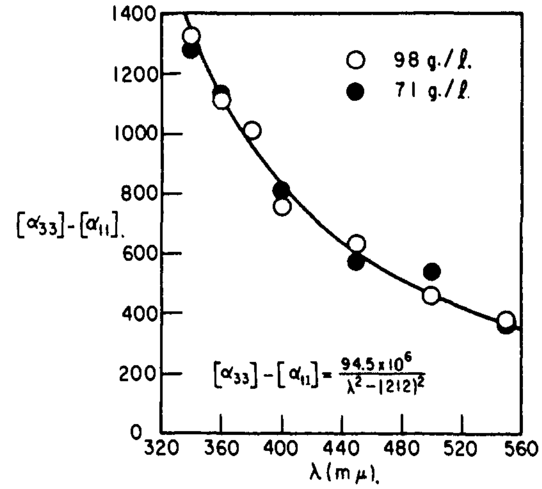

Fig. 3.—The difference in specific optical activity parallel and perpendicular to the helical axis *vs.* wave length for poly-γ-benzyl-L-glutamate in ethylene dichloride. The solid line is a plot of the one term Drude equation given in the figure.

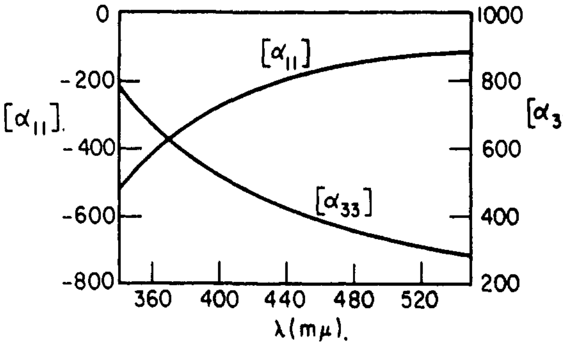

Fig. 4.—The specific optical activity along the helical $[\alpha_{33}]$ and perpendicular to the helical axis $[\alpha_{11}]$ *vs.* wave length.

from this one bit of qualitative information. Unfortunately, this theory does not exist yet. Moffitt[8] has suggested that $[\alpha_{33}] >> [\alpha_{11}]$ for right-handed helices. However, this cannot be accepted as a firm conclusion until final revision[8] of his theory is forthcoming.

The magnitude of $[\alpha_{33}] - [\alpha_{11}]$ and its dispersion is quite informative particularly when compared to $[\alpha]_0 = (2[\alpha_{11}] + [\alpha_{33}])/3$. The value of $[\alpha]_0$ is about +10 at 550 mμ; it decreases with decreasing wave length reaching 0 at 425 mμ and then decreases very rapidly to −95 at 340 mμ.[1,6,15] Therefore the difference in optical activity parallel and perpendicular to the helical axis is at least 10 times larger than the average optical activity. This must mean that the individual optical activities have different signs; their values are shown in Fig. 4. The principal optical activities of macroscopic copper helices also have different signs.[28] For right-handed copper helices $[\alpha_{33}]$ has negative Drude terms while $[\alpha_{11}]$ has positive Drude terms. This information cannot be used to help determine the sense of molecular helices until it is known how the sign of rotation depends on the direction of greatest polarizability of a helical segment.

As mentioned earlier the dispersion data could be fit by a one term Drude equation with λ_0 212 mμ. For theoretical purposes it is better to use the effective molecular rotation introduced by Moffitt[6]

$$[m'] = \left(\frac{3}{n^2+2}\right)\frac{M_0[\alpha]}{100} = \frac{a_0\lambda_0^2}{\lambda^2-\lambda_0^2} \tag{6}$$

The residue molecular weight is M_0 (219 for PBLG); n is the refractive index of the solution. We have approximated n by the Sellmeier equation

$$n^2 - 1 = \frac{1.047\lambda^2}{\lambda^2-(106)^2} \tag{7}$$

The parameters were obtained from refractive index data for ethylene dichloride in the "International Critical Tables." From eqs. 5, 6, 7 we obtain

$$[m'_{33}] - [m'_{11}] = \frac{3{,}570(207)^2}{\lambda^2-(207)^2} \tag{8}$$

We notice that λ_0 has been lowered slightly by the consideration of the dispersion of the refractive index. The corresponding equation for the average optical activity of PBLG in EDC is[6]

$$[m']_0 = \frac{205(212)^2}{\lambda^2-(212)^2} - \frac{635(212)^4}{[\lambda^2-(212)]^2} \tag{9}$$

The values of λ_0 are not quite the same; as λ_0 is determined by a number of absorption bands[7] which contribute differently to eq. 8 and 9, this is not surprising. It is apparent that the individual rotations $[m'_{ii}]$ must each be characterized by a two term equation similar to eq. 9. The special terms however must be nearly equal so as to cancel when the difference (eq. 8) is found.

The anisotropy of the optical activity, $[m'_{33}]$, − $[m'_{11}]$ with its simple wave length dependence should be a better characteristic of helical polypeptides than the dispersion of the average optical activity. As the average involves the difference of two large numbers, we would expect the anisotropy to be much less solvent dependent. For proteins the anisotropy of the optical activity

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(28) I. Tinoco, Jr., and M. P. Freeman, *J. Phys. Chem.*, **61**, 1196 (1957).

should again give more information than the average. The helical content and the orientation of the helices in the molecule should be determinable.

Acknowledgments.—We wish to thank Dr. E. R. Blout for the gift of the PBLG which made this study possible. We also are indebted to Prof. M. Calvin for the use of his laboratory and polarimeter. The help of Prof. C. T. O'Konski and Mr. W. H. Orttung, who made their results available prior to publication, is gratefully acknowledged.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS]

A Kinetic Study of the *n*-Propyl Radical Decomposition Reaction

BY JACK G. CALVERT AND WILLIAM C. SLEPPY

RECEIVED OCTOBER 8, 1958

Thermally equilibrated *n*-propyl radicals were generated homogeneously through the selective photolysis of azomethane at 3660 A. in *n*-butyraldehyde–azomethane mixtures. The decomposition reaction, $n\text{-C}_3\text{H}_7 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$ (1), was followed by measurement of the rate of ethylene formation. The steady-state concentration of *n*-propyl radicals was gauged indirectly by the determination of the rates of butane formation, $\text{CH}_3 + n\text{-C}_3\text{H}_7 \rightarrow n\text{-C}_4\text{H}_{10}$ (5), and ethane formation, $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ (6). From the temperature dependence of the rate function, $R_{\text{C}_2\text{H}_4}R_{\text{C}_2\text{H}_4}{}^{1/2}/R_{n\text{-C}_4\text{H}_{10}} = k_1k_6{}^{1/2}/k_5$ and the assumption $k_6 = k_5 = 2.2 \times 10^{13}$ cc./mole-sec., it is estimated that $k_1 \cong 2.85 \times 10^{15}e^{-34.9/RT}$ sec.$^{-1}$. From these data and Brinton's estimate of k_{-1}, we derive: $\Delta H_1 \cong 26.2$ kcal./mole; $\Delta S_1{}^0 \cong 15.4$ e.u. (near 200°). These and accurate thermal data suggest $D_{\text{CH}_3\text{-H}} - D_{n\text{-C}_3\text{H}_7\text{-H}} \cong 6.8$ kcal./mole; taking $D_{\text{CH}_3\text{-H}} = 102.0$ kcal./mole, $D_{n\text{-C}_3\text{H}_7\text{-H}} \cong 95.2$ kcal./mole. The agreement is good between the present kinetic estimates of the thermodynamic quantities related to reaction 1 and those estimated from "reasonable" thermal data. It is probable that the previous kinetic estimates of $E \cong 19$–21 kcal./mole are seriously in error.

The great divergence between the published kinetic data and "reasonable" thermal data for reaction 1

$$n\text{-C}_3\text{H}_7 \longrightarrow \text{CH}_3 + \text{C}_2\text{H}_4 \qquad (1)$$

is alarming. There are three independent determinations from photochemical and thermal kinetic experiments which suggest $E_1 \cong 19$–21 kcal./mole.[1–3] From measurements of the rate of methyl radical addition to ethylene, the reverse of reaction (1), Mandelcorn and Steacie[4] derive $E_{-1} \cong 7 \pm 1.5$ kcal./mole. Recently a more detailed study of this reaction by Brinton[5] has confirmed the "high" value for E_{-1}; he derives $E_{-1} \cong 8.7$ kcal./mole. Thus current kinetic data suggest $\Delta H_1 \cong E_1 - E_{-1} \cong 10$–$14$ kcal./mole. Contrast this estimate with that based on "reasonable" thermal data, $\Delta H_1 \cong 23$–26 kcal./mole.[6,7] The recent "high" values for E_{-1} appear to be well substantiated, but the accuracy of the kinetic estimates of E_1 should be questioned, as Mandelcorn and Steacie suggest.[4] Indeed the estimates of E_1 seem to be low in view of the recent findings of Trotman-Dickenson and Kerr.[8] The preliminary results of a study of the full arc, high temperature photolysis of *n*-butyraldehyde give: $E_1 \cong 25$ kcal./mole. Recently a re-evaluation of the earlier work relative to reaction 1 has been made,[9] and several possible sources of error have been noted.

The present study was designed to avoid many of the possible complications often encountered in the photochemical studies of radical decomposition reactions. Thermally equilibrated *n*-propyl radicals were generated homogeneously; the thermal decomposition of *n*-butyraldehyde was sensitized by the selective photolysis of azomethane at 3660 Å. in *n*-butyraldehyde–azomethane mixtures. It will be seen that the data from this system remove the apparent conflict between kinetic and thermal estimates of the thermodynamic quantities related to reaction 1.

Experimental

Apparatus.—The photolysis system was similar to that described previously.[10] One significant change was made to obtain a higher light intensity and higher radical concentrations; these conditions favor the desired radical association products, ethane and butane, from which a measure of the *n*-propyl radical concentration may be had. An additional light source (Hanovia Type A, S-500, burner) and 3660 Å. filter system was placed on the optical path, outside the air thermostat, at the rear of the photolysis cell. In the runs at the highest temperatures both the arcs at the front and the rear of the cell were operated at maximum intensity. Under these conditions the rates of ethane and butane formation were sufficiently raised to make analysis for these products feasible, even though the products of the chain reactions, CO, C_3H_8, CH_4 and C_2H_4, were still dominant.

Materials.—Azomethane was prepared and purified as described by Renaud and Leitch.[11] *n*-Butyraldehyde was taken from a volatile fraction of the Eastman White Label product and further purified by bulb-to-bulb distillation at reduced pressure. Standard reference samples of the hydrocarbon gases were Phillips research grade.

Product Analysis.—By combined mass spectrometric and chromatographic analyses, identification of a number of products was made: CH_4, N_2, CO, C_2H_4, C_2H_6, C_3H_6, C_3H_8, $n\text{-C}_4\text{H}_{10}$ and $n\text{-C}_6\text{H}_{14}$. The products were divided into three fractions for convenience in analysis. The first fraction, N_2, CO and CH_4, was pumped off with a Toepler pump while the trap was maintained at liquid nitrogen temperature. This fraction was not analyzed in most of the runs, since these products offered no unique data which would justify the time expenditure required for the analyses.

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