

## Optical Rotatory Power of Organic Solutions in an Electric Field\*

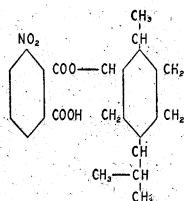
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Andrew McLean, a Scotch chemist, has shown that a relationship exists between the rotatory power of an optically active solution and the electron moment of the solvent. It has been found that in general the rotation varies in the opposite sense to the electric moment of the solvent throughout a series of solvents derived from the same parent hydrocarbon. An explanation of this observation has been advanced in terms of dipolar association between solvent and optically active solute and numerous results have been brought forward in support of this hypothesis.

These observations suggested the possibility that an electric moment induced in the solvent molecules by an external  $E$  might have an effect similar to that of the permanent moment.

*First Experiments.*—Previous experience had shown that solvent influences are best observed with optically active components of simple molecular structure with a strongly polar group situated near the asymmetric center. For this reason 21-menthyl-3 nitrohydrogen phthalate was considered a suitable optically active solute.



Since the moment induced in the solvent molecule by an external  $E$  is likely to be small compared with that due to the introduction of a polar substituent, it was thought that solvents with zero or very small permanent electric moment would be most advantageous for the proposed investigation. Accordingly benzene and toluene were employed as solvents. Fig. 1 gives the experimental arrangement. We filled the polarimeter tube with a 3 per cent solution of menthylester, applied a field of about 6,000 volts per cm, and rotated the tube through an angle of  $180^\circ$ . Results are shown in Fig. 2 which is a sine curve. Previous observations have shown that the Kerr effect was not present. The Kerr effect is independent of the direction of the electric force and its magnitude is proportional to the square of the electric intensity. Curves in Figs. 3 and 4 show the complicated effect of  $E$ . It could not always be repeated. Finally it was found that these solutions had a very slight turbidity. They were filtrated through very fine filter paper and then the effect disappeared completely.

\* Published posthumously. Prof. Kunz died before he could present this paper at the annual meeting. In fact it had not yet been put into typed form at the time of his death. The Academy is honored to publish one of the last works to come from his hand, and hereby acknowledges indebtedness to Prof. J. T. Tykociner for his aid in carrying it through to publication.

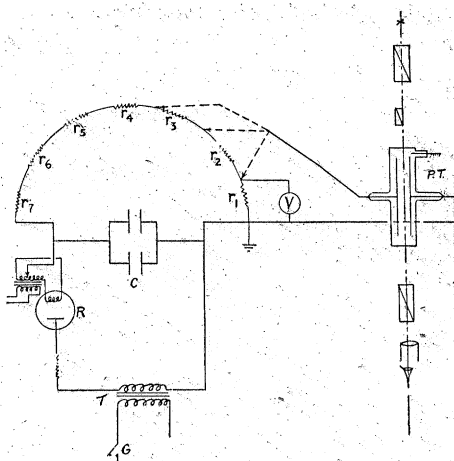


FIG. 1

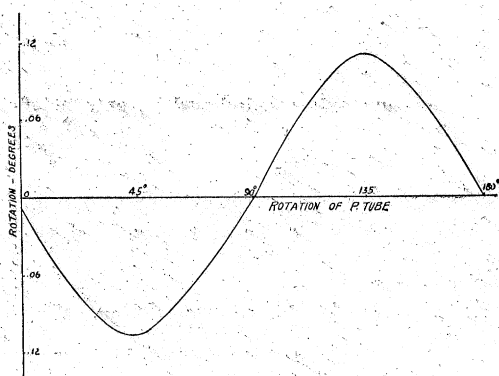


FIG. 2

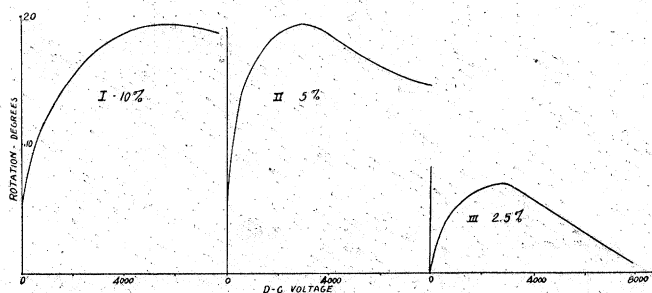


FIG. 3

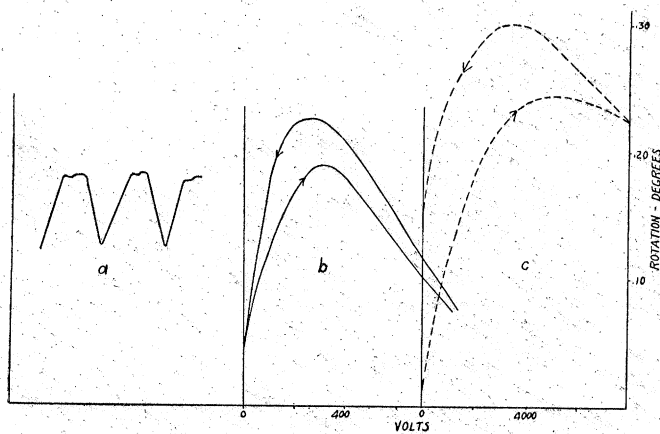


FIG. 4

*Theory.*—Molecules are either permanently polarized, polar molecules.

$$\mu_T = \frac{F\mu^2}{3kT}$$

or moments are induced by external field.

$$\mu_D = \frac{e^2 F}{f}$$

$$\mu = \mu_T + \mu_D = \alpha F = F \left( \alpha_0 + \frac{\mu^2}{3kT} \right)$$

$$I = n\mu = n\alpha F = n\alpha \left( E + \frac{4\pi I}{3} \right) \quad (1)$$

$$D = E + 4\pi I = kE$$

$$I = \frac{D - E}{4\pi} = \frac{E(k - 1)}{4\pi} \text{ substitute in (1)}$$

$$\frac{E(k - 1)}{4\pi} = n\alpha E \left( 1 + \frac{4\pi}{3} \left( \frac{k - 1}{4\pi} \right) \right)$$

$$k - 1 = n\alpha \frac{4\pi}{3} \left( 1 + \frac{k - 1}{3} \right) = \frac{n\alpha 4\pi}{3} (3 + k - 1)$$

$$= n\alpha \frac{4\pi}{3} (k + 2)$$

$$\frac{k - 1}{k + 2} = \frac{4\pi}{3} n\alpha \frac{M}{\delta} \quad \begin{array}{l} M = \text{molecular weight} \\ \delta = \text{density.} \end{array}$$

$$\frac{k - 1}{k + 2} \frac{M}{\delta} = \frac{4\pi}{3} n\alpha \frac{M}{\delta} \frac{nM}{\delta} = N = 6.06 \cdot 10^{23}$$

$$\frac{k - 1}{k + 2} \frac{M}{\delta} = \frac{4\pi}{3} \alpha N = P = \text{molecular polarization}$$

for a sphere  $\alpha = a^3$ , and

$$P = \frac{k - 1}{k + 2} \frac{M}{\delta} = \frac{4\pi}{3} a^3 N = \text{volume of molecules in gm. mol., but in general}$$

$$P = \frac{4\pi}{3} N \left( \alpha_0 + \frac{\mu^2}{3kT} \right) \quad P_0 = \frac{4\pi}{3} N \alpha_0$$

$$P - P_0 = \frac{4\pi}{3} N \frac{\mu^2}{3kT} \text{ for high frequencies,}$$

the polar part disappears and  $k = n^2$  and

$$P_0 = \frac{n\pi}{3} N \alpha, \quad \alpha = \frac{3P_0}{4\pi N} \text{ and } P_0 = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\delta}$$

This determines  $\alpha$ , finally

$$\mu = \alpha \cdot F$$

$$F = E \cdot 1.4 \quad E = 66$$

$$F = 93$$

$$\mu = 1.02 \cdot 10^{-28} \cdot 93 = 9.5 \cdot 10^{-28}$$

$$[M] = \frac{M}{100} [\alpha]$$

$$[\alpha] = \frac{\alpha}{1 E \delta}$$

$$\text{C}_6\text{H}_5\text{NO}_2 : \mu = 3.89 \cdot 10^{-18} \\ [M] = 423$$

$$\text{C}_6\text{H}_5 : \mu = 9.5 \cdot 10^{-22} \\ [M] = 543$$

the difference  $543 - 423 = 120$  is due to the moment of  $\text{NO}_2$  group which is  $3.89 \cdot 10^{-18}$

$$120^\circ : 3.89 \cdot 10^{-18} = x^\circ : 9.5 \cdot 10^{-22} \\ x = 0.0293 = \text{molecular rotation} \\ = [M]$$

$$[\alpha] = \frac{[M] 100}{M} = 0.0376$$

$$\alpha = [\alpha] 1 E \delta = 0.00108^\circ$$

hence our fields were too weak even for  $E = 20,000$  volts/cm.

*New Experiments.*—The experiment was repeated with stronger A.C. field up to 65,000 volts per cm. A straight line shown in Fig. 5 is obtained according to the theory while the Kerr effect gives a parabola, Fig. 6, which we have obtained for  $\text{CS}_2$ .

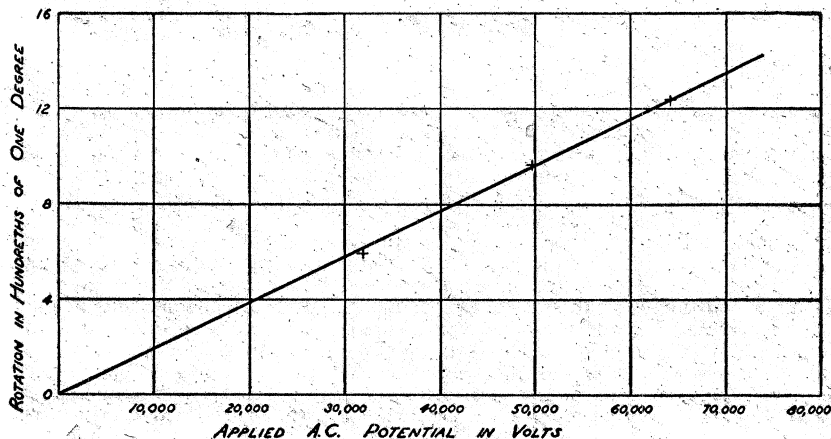
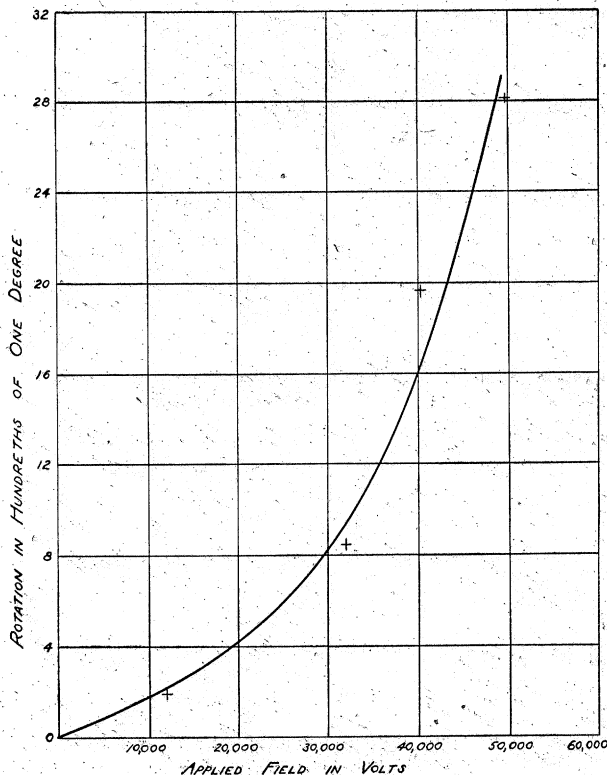


FIG. 5 ROTATION VS. ELECTRIC FIELD

5% SOLUTION OF MENTHYL ESTER-TRI-NITRO. PHTHALIC ACID IN BENZENE

FIG. 6 KERR EFFECT WITH  $CS_2$ .

*Special Observations.*—1. After this solution, which gave the straight line, had been standing several days (16 days) then, if the field is thrown on, the polarization changes slightly. When the field is taken off, the other side of the field of sight in the polariscope becomes very dark, and then changes gradually to zero. The change amounted to as much as one degree.

2. The optically inactive compound of ethylester was dissolved in toluene. The solution was made by heating the ester and toluene, and while hot, poured into the tube. There again when a field was applied a rotation was obtained, as functions of  $E$ , reaching a maximum at about 3,000 volts. It was difficult to repeat these results as the solution seemed to change continuously during the experiment. With the same field strength the polarimeter readings were very erratic, e.g., at one observation the application of a field of 14,300 volts caused an instantaneous rotation of  $3^\circ$ , but in a few seconds, whilst the field was still on, it dropped to  $0.35^\circ$ . After the solution had been standing for 3 days even the most powerful field had no effect on it. However, with a fresh hot solution rotational changes were again observed.

*Summary:* Various optically active menthyl compounds have been subjected to an electric field. No Kerr effect has been observed. It was found that the rotation of the plane of polarization depends on the angle between that plane and the lines of the external electric field. The rotation of the plane of polarization is a linear function of the field strength in agreement with the developed theory and quite different from the Kerr effect.