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The Effect of Solvents on the Optical Rotation of Propylene Oxide

Yoshiyuki KUMATA, Junji FURUKAWA and Takayuki FUENO*1

Department of Synthetic Chemistry, Kyoto University, Kyoto

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It is known that the rotation of an optically active substance is varied according to the nature of the solvents. The so-called "rotivity", Ω, which is the rotation corrected for the refractive index of the solvent used, has been defined by the equation:[1]

$$3\Omega = \frac{3}{n^2+2}[\alpha]$$

where n, $[\alpha]$ and $3/(n^2+2)$ are the refractive index, the specific rotation and the Lorentz factor, respectively. This paper deals with the effect of solvents on the rotivity of propylene oxide.

Experimental

The solvents were selected widely from a stand point of chemical structure, dipole moment, dielectric constant and refractive index. Each solvent was purified by a conventional method. The optical rotation was measured by using a JASCO polarimeter Model ORD, UV-5 and a Yanagimoto polarimeter (OR-10) at ambient temperature. The concentration of propylene oxide in various solvents was fixed at 5.00 g/100 ml.

Propylene oxide was synthesized according to a fermentation method.[2] The specific rotation of the propylene oxide was +12.53° (neat, at 16°C).

Results and Discussion

The specific rotation, $[\alpha]_D$, and the rotivity multiplied by three, 3Ω, of propylene oxide observed in various solvents are listed in Table 1. Although the rotivity is said to be the specific rotation corrected for the refractive index of the solvents used, it still depends on solvent, as may be seen in Table 1. The tendency of this variation of rotivity with solvent is the same as that of the rotational strength of a steroidal compound.[3]

The rotivity data listed in Table 1 appear to show that the 3Ω value of propylene oxide tends to decrease with the increasing polarity of solvent. In Fig. 1 the 3Ω values are plotted against the solvent Z-values,[4] wherever available. Although the plotted points are somewhat scattered, there does seem to be a correlation between the two quantities.

Figures 2 and 3 are the plots of the 3Ω value of

TABLE 1. SPECIFIC ROTATION OF (R)-PROPYLENE OXIDE IN VARIOUS SOLVENTS

	Solvent	$[\alpha]_D$	$\frac{3[\alpha]_D}{n_D^2+2}$
A	Benzene	30.6	21.6
B	*N*,*N*-Dimethylaniline	29.0	19.6
C	Anisole	26.4	18.4
D	Tetrachloroethylene	20.1	14.1
E	Carbon disulfide	19.4	12.5
F	Chlorobenzene	19.4	13.5
G	Carbon tetrachloride	18.7	13.6
H	Hexamethylphosphoric triamide	18.4	13.4
I	Pyridine	18.1	12.7
J	*p*-Dioxane	18.0	13.4
K	*o*-Nitroanisole	17.7	12.0
L	Diethyl ether	17.0	13.3
M	Triethylamine	17.0	12.9
N	Nitrobenzene	16.4	11.2
O	Methylene iodide	15.6	9.3
P	*n*-Pentane	14.3	11.2
Q	*N*-Methylacetamide	14.1	10.5
R	Tetrahydrofuran	13.7	10.3
S	Ethyl acetate	13.1	10.1
T	*N*,*N*-Dimethylformamide	12.9	9.6
U	Dimethylsulfoxide	12.8	9.2
V	Cyclohexane	11.9	8.8
W	Aniline	11.9	7.9
X	Benzonitrile	9.4	6.5
Y	Chloroform	8.5	6.2
Z	Acetone	8.2	6.4
a	Ethanol	7.9	6.2
b	Cyclohexanone	7.9	5.8
d	Methanol	7.2	5.7
e	Acetonitrile	6.0	4.7
f	1,2-Dichloroethane	5.8	4.3
g	Methylene chloride	5.5	4.1
h	Nitromethane	5.0	3.8
i	Acetic acid	2.0	1.5
j	Water	−4.3	−3.4

*1 Present address: Faculty of Engineering Science, Osaka University, Toyonaka, Osaka.

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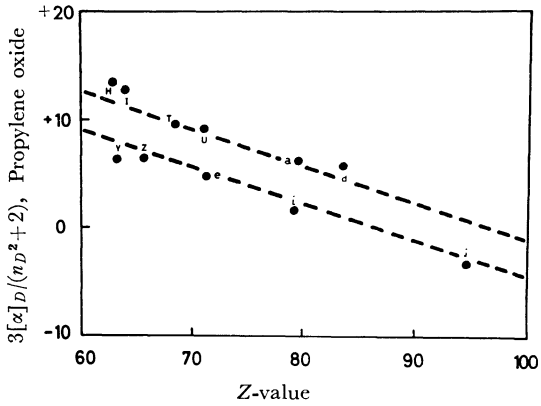

Fig. 1. Z-value *vs.* three times of rotivity.

propylene oxide against other polarity parameters of solvent, $(\varepsilon-1)/(\varepsilon+2)$ and E_T-value,[5] respectively. Addmittedly, these correlations of the rotivity with the various polarity parameters of solvent are poor, they will suffice to indicate a general trend. Thus, with increasing polarity of solvents, the rotivity may be continuously decreased until it may take on a value minus in sign. By this token, therefore, a change in the direction of optical rotation in differing solvents may well be something not abnormal, although it may certainly be an affair encountered only in limited cases.

In any discussion of solvent effects, it seem to be very important to consider the shape of cavity,[6,7] the anisotropy of the polarizability of solute[8,9]

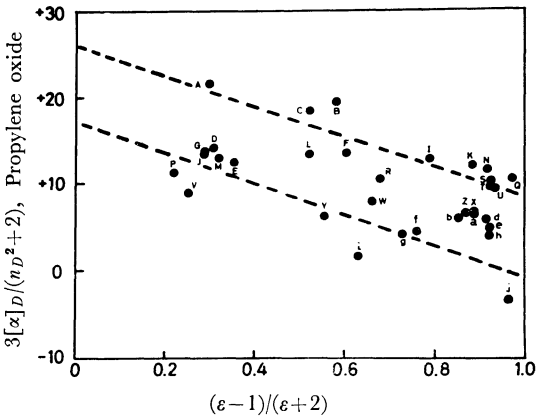

Fig. 2. $(\varepsilon-1)/(\varepsilon+2)$ *vs.* three times of rotivity.

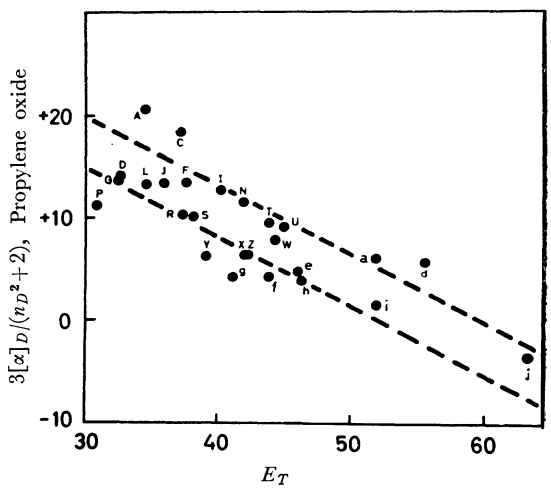

Fig. 3. E_T-values *vs.* three times of rotivity.

and the orientation of solvents to solute.[10,11] However, because the solvent effect on the optical rotation reflects a dynamical electromagnetic interaction between the dielectric groups of solute and solvents which have polarizability tensors, it will in general be extremely difficult to represent the effect with any simple parameter of solvents.

In Fig. 4, the effect of solvents on the optical rotatory dispersion of propylene oxide is shown. It should be noted that even a substance like propylene oxide, which has a rigid three-membered-ring and hence is incapable of changing its conformation in different solvents, shows an anomalous dispersion curve.

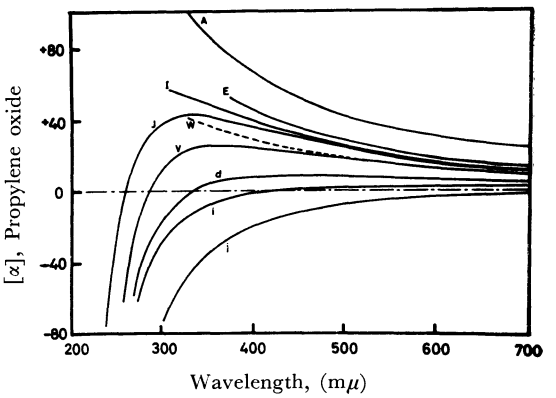

Fig. 4. Optical rotatory dispersion curve of (R)-propylene oxide in several solvents.

All the results described above would combine to give a serious warning against interpreting the optical behaviors of active substances in different solvents directly from their conformational change. Such interpretations might not be valid in general cases and would often be merely illusory.

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