

l-menthylate, it was titrated with sodium triphenylmethyl. This solution was then measured in the polarimeter and the specific rotation for sodium *l*-menthylate was found to be $[\alpha]^{25}_D -12.2 \pm 0.6$. Patterson and Taylor¹⁰ give the specific rotation of menthol as $[\alpha]^{25}_D -45.57$.

An ethereal solution of menthol was successively diluted from 1 to 0.0125 *M*, and no change was observable in the specific rotation.

Patterson and Taylor¹⁰ have shown that *l*-menthol in benzene is "practically insensitive to temperature change." With the menthylate solution, a 0.003° change in rotation was observed for every degree change in temperature. In the same way, the temperature effect on the equilibrium of a reaction is from 0.001 to 0.003° change in rotation per degree temperature change. Since the polarimetric room was thermostatted to $24.5 \pm 1.5^\circ$, the maximum change in rotation due to temperature change is less than the experimental error.

Since the specific rotation of both pure menthylate and menthol is known, it is only necessary to know, in a given solution, the total concentration of menthol, either as menthol or menthylate, and a measurement of the rotation gives the concentrations of both. The total concentration was found by weighing the amount of pure menthol used and measuring the benzene volumetrically.

The rates of these metathetical reactions were all practically instantaneous. In the measurement of benzhydrol, three to five minutes after adding the benzhydrol, the reaction had reached a value that did not change after one and one-half hours. A second reading after at least one-half hour had elapsed was taken on tertiary amyl alcohol, tertiary butyl alcohol, isopropyl alcohol and acetophenone, and no change was observed. Of the remaining compounds, precipitates appeared with methyl alcohol and phenylfluorene which took quite a while to settle (one to two hours) and only on benzyl alcohol was no second reading taken after some time had elapsed. So with no alcohol was a shift in the rotation observed. The rate of the reaction was faster than could be detected.

(10) Patterson and Taylor, *J. Chem. Soc.*, **87**, 122 (1905).

Since most of the sodium salts of the alcohols are fairly insoluble in benzene, it was necessary to prevent their formation as much as possible. This was done by using smaller and smaller amounts of alcohol and menthylate and larger and larger quantities of menthol, until no precipitate formed. This was not always successful, and the accuracy of the readings was reduced. When the menthol was used in solution to partially block the reaction, a small amount of menthylate was also present in the solution in order to be sure that there was no contaminating substance present.

Solubility of Sodium Methylate in Benzene.—A 100-cc. flask was filled with benzene under nitrogen and a large amount of sodium wire was added. One-half cc. of methyl alcohol was added against a current of nitrogen. A rapid reaction occurred. The flask was left for two days, after which three samples were removed and titrated with 0.01 *N* hydrochloric acid, using phenolphthalein as an indicator. The value for the solubility was found to be 0.3 to 0.9 of a millimole per liter. A correction was then made for the dissolved sodium hydroxide. The solubility was determined by sealing sodium hydroxide, sodium and benzene in a small flask and shaking overnight. The solution was titrated and found to contain 0.1 millimole of sodium hydroxide per liter of benzene.

Summary

1. Fifteen weak acids have been measured colorimetrically and inserted in a table of acids of decreasing strength. Eight other weak acids have been investigated by this method.

2. Ten weak acids have been measured spectroscopically by an indicator method that is described.

3. The acidity of six alcohols, one enol and one hydrocarbon have been determined by a polarimetric method that is described.

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The Diffraction of X-Rays by the Higher Polyethylene Glycols and by Polymerized Ethylene Oxides¹

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In recent studies² Hibbert, Perry and Pullman have obtained very strong evidence in support of the suggestion³ that polymerized ethylene

(1) This paper constitutes No. LI in the series of "Studies on Reactions Relating to Carbohydrates and Polysaccharides," by Dr. Harold Hibbert and co-workers.

(2) Hibbert and Perry, *Can. J. Research*, **8**, 102 (1933); Perry and Hibbert, *ibid.*, **B14**, 77 (1936). The method of preparation, the constitution and the physical and chemical properties of the higher polyethylene glycols and polymerized ethylene oxides will be discussed in forthcoming articles by Pullman and Hibbert.

(3) (a) Staudinger and Schweitzer, *Ber.*, **62**, 2395 (1929); (b) Carothers, *Chem. Rev.*, **8**, 391 (1931); (c) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932, p. 287.

oxides probably have the same composition as the polyethylene glycols (*i. e.*, HOCH₂CH₂(O-CH₂CH₂)_xOCH₂CH₂OH). Since the former already have been subjected to x-ray examination,⁴ and since specimens of polymerized ethylene oxides and polyethylene glycols of comparable molecular weights⁵ were available, an opportunity was presented for a comparison of the diffraction

(4) Sauter, *Z. Physik. Chem.*, **B21**, 161-185 (1933).

(5) Molecular weights stated throughout this paper refer to values in solution as determined by Staudinger's viscosity methods,³⁰ p. 56 *et seq.*

of x-rays by the polymerized ethylene oxides and polyethylene glycols prepared by Pullman and Hibbert² and a comparison of these data with those for the polymerized ethylene oxides examined by Sauter.⁴

Sauter^{4,6} has studied polymerized ethylene oxides of molecular weights 2400, 3100, 8000, 13,000, 16,000, 33,000, 55,000 and 100,000, respectively. The last, which is reported⁴ to be a rubber-like substance, enabled him to obtain fiber diagrams by stretching the specimen, so that most of his work was confined to this polymer. Powder diagrams of all specimens, however, were identical (at least without photometric or ionization measurements) both as to positions of haloes and relative intensities.

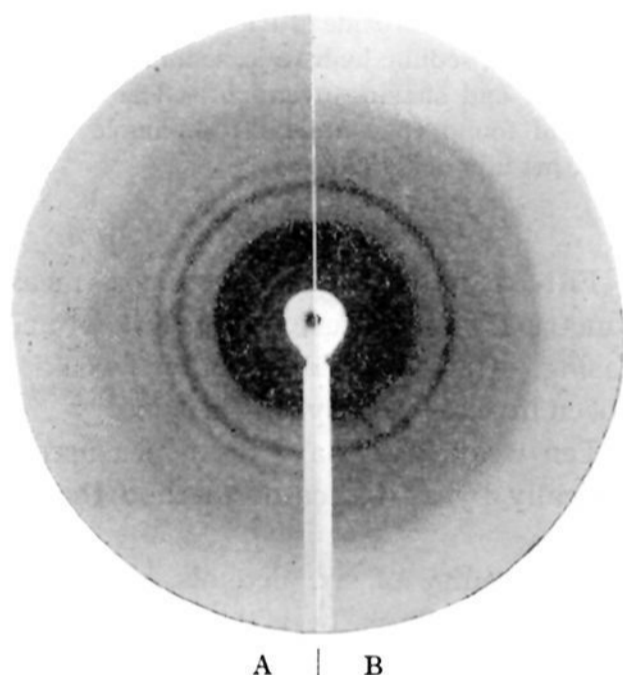


Fig. 1.—A, Polymerized ethylene oxide; B, polyethylene glycol.

As none of the polymers available for the present investigation were high enough to possess any appreciable elasticity the present paper is concerned solely with powder diagrams. Copper radiation ($\lambda = 1.54 \text{ \AA.}$), filtered through nickel foil to remove the K_{β} line, was employed with a crystal-to-plate distance of 2.25 cm.

The specimens of Pullman and Hibbert² selected for study were the 54 and 162-membered polyethylene glycols and the corresponding polymerized ethylene oxides (mol. wts. 3000 and 6500). Preliminary photographs having given essentially identical diagrams for all four specimens, and shown that very long exposure times would be necessary for accurate identification and measure-

ment of the weaker haloes, a detailed examination

(6) See Staudinger,²⁰ p. 294.

of the 162-membered polyethylene glycol and the polymerized ethylene oxide of molecular weight 3000 (corresponding to the 54-membered polyethylene glycol) was undertaken.

A typical composite negative for these two specimens is reproduced in Fig. 1. Due to the pronounced background fogging (particularly in the case of the glycol) and to the excessive range of densities in the original negatives some difficulty was experienced in obtaining reproducible prints. The authors are indebted to Mr. H. Rudoff, graduate student in the Department of Chemistry, McGill University, for technical assistance in this connection.

The detailed results of the x-ray examination are summarized in Table I. The first and second columns give the numbers of the diffraction effects and the corresponding values of $\sin \theta$, respectively, from Table I of Sauter's paper.⁴ Corresponding values of $\sin \theta$ for the polymerized ethylene oxide of molecular weight 3000 and for

TABLE I

SUMMARY OF RESULTS

No. (S)	$\sin \theta (\lambda = 1.54 \text{ \AA.})$			I		
	(S)	(O)	(G)	(S)	(O)	(G)
1	0.106	v.w.
2	.117	w.
3	.121	v.w.
4	.133	0.131	0.131	w.	w.	w.
5	.138	v.w.
6	.163	.166	.166	v.w.	v.s.	v.s.
7	.169			v.s.		
8	.196	.202	.202	w.	v.s.	v.s.
9	.205			m.		
10	.208	.231	.233	v.s.	s.	s.
11	.221			w.		
12	.229	.270	.270	m.	w.	w.
13	.234			m.		
14	.237	.284	.284	w.m.	v.w.	v.w.
15	.243			w.		
16	.270	.309	.309	w.in.	s.	s.
17	.283			m.		
18	.308	.342	.340	m.	m.	w.
19	.308			m.		
20	.308	.355	.355	m.w.	..	v.w.
21	.316			m.		
22	.344	.369	.369	m.	w.	w.
23	.358			w.		
24	.372	.388	.388	w.	w.	w.
25	.372			w.		
26	.390	.417	.418	w.	w.	w.
27	.407			v.w.		
28	.418	.454	.454	v.w.	v.w.	v.w.
29	.428			v.w.		
30	.460	.483	.483	v.w.	v.v.w.	..
31	.460			v.w.		
32	.482	v.w.	v.v.w.	..

the 162-membered polyethylene glycol are shown in columns three and four, respectively. Visually estimated intensities⁷ are recorded in columns five (from Sauter's paper⁴), six (for the oxide), and seven (for the glycol), respectively.

In connection with the foregoing table the following remarks may be noted. Sauter's lines 1 and 2 apparently are present in traces on the best negatives for the oxide and glycol obtained in the present study but are too weak in intensity for measurement. Lines 3 and 5 would fall within about 0.2 mm. of the inner and outer edges of line 4 so that they would practically be unresolvable for the crystal-to-plate distance employed. The remainder of the data, however, appeared to be conclusive enough not to warrant the long exposure times necessary to bring out lines 1, 2, 3 and 5 at a longer crystal-to-plate distance. Certain groups of diffraction effects in Sauter's table appear as bands in the powder diagrams. In Table I these have been bracketed and the mean position of the observed band is given in columns 3 and 4. For example, Sauter's numbers 11, 12, 13, 14, 15 have $\sin \theta$ values which would result in haloes falling within the inner and outer edges of the band on the present oxide negative whose mean position is given by a $\sin \theta$ value of 0.231. Finally the very weak halo at $\sin \theta = 0.482$ (Sauter's No. 32) is present in the best negative for the glycol but is not included in Table I because it is too weak in intensity for accurate measurement.

The general agreement among Sauter's data for polymerized ethylene oxides, and the present

data for the polymerized ethylene oxides and polyethylene glycols prepared by Pullman and Hibbert is very satisfactory. The only anomalous features are the absence of line 23 from the present polymerized ethylene oxide negatives, and the definitely stronger relative intensity of line 22 in the oxide compared with the glycol photographs. In this connection, however, it should be noted that line 23 is of weak intensity and is, moreover, clearly present on the glycol negatives. These features may be purely fortuitous or may have something to do with the relative physical characteristics of the samples. In general the glycols are more hygroscopic than the corresponding oxides, probably because the former comprise only one polymeric species while the latter probably contain appreciable fractions of higher (less hygroscopic) polymers. In comparing the relative intensities of Sauter with those observed in the present investigation it must also be borne in mind that the former were estimated on fiber diagrams whereas the latter were obtained from powder diagrams.

A consideration of the data presented in Table I, and a comparison between Fig. 1 of this paper and Fig. 2 of that of Sauter,⁴ leads to the conclusion that, in so far as the diffraction of x-rays is concerned, there is no essential difference either between the polymerized ethylene oxides and the polyethylene glycols prepared by Pullman and Hibbert or between these and the polymerized ethylene oxides prepared by Lohmann for Sauter's investigation.

(7) m. = medium; s. = strong; v. = very; w. = weak.

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A New Reagent for Structure Determination

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In the identification of organic compounds those tests are especially valuable which can be carried out quickly on small amounts of material and which show, by the production of a color or precipitate, the presence of a specific group or structure. In work with active methylene compounds it has often been desirable to have a reliable *general* test for such substances. The production of colors with ferric chloride solution

is limited in usefulness because many active methylene compounds (for example, the malonic esters) do not react with this reagent. The present paper describes a test which has frequently been of value and which, under the conditions specified later, is general for substances which contain hydrogen on a carbon atom bearing at least *one* acyl group or *two* other activating groups.

The test consists of the addition of an alcoholic solution of mercuric chloride to a solution of the unknown in alcohol containing sodium ethoxide.

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