

### Asymmetric Dialysis of Racemates

THE enantiomorphous forms of optically active compounds can, as a rule, be differentiated by living membranes and epithelia<sup>1</sup>. To establish the basic mechanisms of such asymmetric resolution, we have carried out experiments with artificial membranes of optically active material. As early as 1928, Keeser<sup>2</sup> demonstrated asymmetric diffusion; blocks of gelatine swelled better in solutions of the D-form of tartaric acid, cinchonine and epinephrine than with the L-enantiomorphs. It is therefore surprising that such properties as asymmetric resolution do not seem to have been demonstrated with well-known membranes, even if the membranes consisted of asymmetrical material such as 'Cellophane' or collodion (products of cellulose), or of the fresh mucosa of intestinal loops (products of proteins)<sup>3</sup>, etc.

We tried to increase the asymmetry of the membrane by enriching it with optically active substances. A 4 per cent collodion solution in ether and ethyl alcohol was added to different alkaloid bases or their acetic or hydrochloride salts and poured out to become membranes. Water was kept on one side of the membrane, and a racemic acid, which is usually resolved by means of the base, on the other. But the measured rotations of the aqueous solutions were not sufficient for an asymmetric dialysis.

The best results were obtained with tartaric acid. As basic substance we used 2-(D-gluco-D-gulo-heptohydroxyhexyl)-benzimidazole, which is one of the best substances for the resolution of tartaric acid<sup>4</sup>. This glucoheptonic acid benzimidazole was dissolved in a 4 per cent alcohol-ether solution of collodion at about 35° C. and acidified with hydrochloric acid. With this membrane we obtained from D,L-tartaric acid a dialysed aqueous solution with a small rotation indicating optically active tartaric acid. We are attempting to improve this interesting method with a multiplicator procedure ('Multiplikator-Verfahren', see ref. 5).

Replacing the collodion membrane with 'Cellophane' dialyser tubing, another form of asymmetric dialysis was possible. If D-, L- and D,L-tartaric acid respectively was put into three tubes, together with the glucoheptonic acid benzimidazole (Table 1), the L-form was bound as a diastereomeric salt, and so the D-tartaric acid dialysed more quickly into the water phase, as was shown in experiments with the D- and D,L-forms. The rotation was about ten times greater than the experimental error. The total tartaric acid transferred was determined acidimetrically.

Table 1. ASYMMETRIC\* DIALYSIS OF TARTARIC ACID AND GLUCOHEPTONIC ACID BENZIMIDAZOLE AGAINST WATER THROUGH A 'CELLOPHANE' MEMBRANE

Procedure: Three portions of 0.9 gm. glucoheptonic acid benzimidazole dissolved in 20 ml. of a 1.25 per cent solution of D-, D,L- and L-tartaric acid and filled into 'Cellophane' tubing; dialysis against 40 ml. water, at 20° C.; in the outer fluid  $\alpha_D^{20}$  was measured in a 200-mm. tube and afterwards 3.0 ml. was titrated with 0.1 N sodium hydroxide against phenolphthalein

Time in min.	D-Tartaric acid		D,L-Tartaric acid		L-Tartaric acid	
	Outside	Inside	Outside	Inside	Outside	Inside
Rotations						
0	0°	+1.93°	0°	+0.85°	0°	+0.09°
30	+0.14°		+0.06°		+0.02°	
160	+0.23°		+0.10°		+0.07°	
180	+0.74°	+1.04°	+0.24°	+0.56°	+0.08°	+0.15°
Acidimetric control						
180	1.42 ml.		1.52 ml.		0.97 ml.	

Table 2. Conditions and arrangement as in Table 1. 0.31 gm. D,L-tartaric acid and 0.23 gm. glucoheptonic acid benzimidazole dissolved in water to an end volume of 10 ml. as inner liquid; outside liquid is 20 ml. water

Time	Rotation	
	Outside	Inside
0 min.	0°	+0.45°
60 min.	+0.07°	
180 min.	+0.14°	
15 hr.	+0.18°	+0.11°

In another experiment with longer duration of dialysis, the asymmetric separation was also found (Table 2). The rotation in the outside liquid increased from 0° to +0.18°, and decreased in the liquid inside from +0.45° to +0.11°. These differences are in good agreement within experimental error, if the rotation of the outside liquid is doubled on account of its doubled volume.

The semipermeable character of the 'Cellophane' membrane was controlled by the method of Wo. Ostwald<sup>6</sup>. Alkaline blue and congo red did not diffuse, congo rubin slightly, methyl violet considerably better.

Hence in the asymmetric dialysis of D,L-tartaric acid, D-tartaric acid is transferred through the membrane because L-tartaric acid forms a less dissociable salt with benzimidazole; so the remaining D-form is more readily transmitted.

V. O. G. KLINGMÜLLER  
G. GEDENK

Physiologisch-Chemisches Institut der Universität,  
Hamburg 20.  
Nov. 13.

<sup>1</sup> Klingmüller, V. O. G., 19th Internat. Physiol. Congr., Montreal, 1953. Klingmüller, V., and Bückmann, F., *Biochem. Z.*, **327**, 450 (1956). Klingmüller, V., and Brune, G., *ibid.*, **328**, 352 (1956).

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<sup>4</sup> Hudson, C. S., Hartley, O., and Purves, C. B., *J. Amer. Chem. Soc.*, **56**, 1248 (1934). Haskins, W. T., and Hudson, C. S., *ibid.*, **61**, 1266 (1939).

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<sup>6</sup> Ostwald, Wo., "Kleines Prakt. f. d. Kolloidchemie", 9. Aufl. (Theod. Steinkopf, Leipzig, 1943).

### High-Intensity Flash Irradiation of Polymers

IN an attempt to shorten exposures in the ultra-violet irradiation of polymers, we have used as light sources high-intensity flash discharge lamps, described by Murphy and Edgerton<sup>1</sup>, which have been used extensively in flash spectroscopy<sup>2-4</sup> and flash photolysis<sup>5,6</sup>. The lamps used were similar to Christie and Porter's fused silica spiral lamp No. III<sup>7</sup> and usually were flashed with 648  $\mu$ f. at 4,000 V. (5,184 j.). Each flash lasted about three milliseconds, and by uranyl oxalate actinometry<sup>8</sup> was shown to yield  $9.6 \times 10^{19}$  quanta in the 2000-4900 Å. region. The polymers were placed approximately along the axis of the lamp coil, either in fused silica or 'Pyrex' glass test-tubes, and were irradiated in air, streaming nitrogen, or *in vacuo*. In several polyethylenes, polystyrene, polyethylene terephthalate, polyisobutylene, 6-10 nylon, polyvinylchloride, polytetrafluoroethylene, regenerated cellulose and cellulose acetate, we found that, in addition to some minor homogeneous photolysis, a single flash caused violent heterogeneous decompositions within the polymer matrices. These decompositions usually were accom-