800,000 the figures are several times less. Thus, for natural rubber $M_n = 193,000$ instead of 830,000, but for synthetic rubber $M_n = 68,000$ instead of 73,000. This result is in good agreement with data in the literature.

One can compute, on a model of an elongated ellipsoid, the length $l = 2b$ of the particles from the values of M and b/a . For natural rubber we obtain in this way $l = 3500$ Å., whereas from the depolarization of diffuse light l was found to be 3400 Å. for the same system (0.1 per cent solution of natural rubber in carbon tetrachloride).⁷ Thus it appears that Polson's method can be applied to linear polymers over a wider range than might have been theoretically presumed.

All the rubber samples studied are characterized by an appreciable excess of the maximal ordinate of the normalized experimental diffusion curve over the ideal curve (this appears also from Fig. 1), thereby indicating polydispersity of these substances. Grálén⁸ suggested a convenient method of quantitative estimation of polydispersity as characterized by the ratio of the diffusion coefficients D_2/D_1 computed from the standard deviation and from the maximal ordinate of the diffusion curve. For a monodisperse substance, $D_2 = D_1$ or $D_2/D_1 = 1$; for natural rubber we have found $D_2/D_1 = 1.17$, after a twofold precipitation $D_2/D_1 = 1.18$, after thermal destruction $D_2/D_1 = 1.72$, etc. Assuming the logarithmic course of the distribution curve, one can, after Grálén, calculate from D_2/D_1 complete distribution curves (Fig. 2), and thus obtain a more demonstrative picture of polydispersity of the substance. Finally, it can be shown that in the general equation for asymmetrical particles, $M = -R/D^2$, the value of a for natural rubber is 1.1 (for nitrocellulose Grálén obtained $a = 1.2$); whence it follows that for linear polymers the change of D follows very closely the change in the molecular weight.

On the whole, the application of the above methods to the rubber-like polymers enables one to obtain from the diffusion and viscosity measurements a fairly complete molecular characterization of these substances. This is particularly significant for laboratories which do not possess an ultracentrifuge.

A full account of this work will be published in the near future in *Acta physicochim. USSR*.

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¹ Lamm, O., *Nova Acta Reg. Soc. Scient. Uppsala*, **10**, No. 6 (1937).

² Simha, R., *J. Phys. Chem.*, **44**, 25 (1940). Mehl, J., Oncley, J., and Simha, R., *Science*, **92**, 131 (1940).

³ Campbell, H., and Johnson, P., *Trans. Farad. Soc.*, **40**, 221 (1944).

⁴ Frenkel, J., *Acta physicochim.*, **19**, 51 (1944).

⁵ Polson, A., *Koll. Z.*, **88**, 51 (1939).

⁶ Cited in Davis and Blake, "The Chemistry and Technology of Rubber" (1937), 232.

⁷ Gehmann and Field, *Ind. Eng. Chem.*, **29**, 793 (1937).

⁸ Grálén, N., *Koll. Z.*, **95**, 188 (1941).

Mechanism of the Beckmann Rearrangement

THE recent resurgence of interest in the mechanism of the Beckmann change reflects the perennial fascination which this subject has for chemists. First, Higman¹ and LeFevre² have suggested that the cation (I) rearranges by rotation of the central pair $>C=N<$ through 90° to form (II).

Such a mechanism, as Dewar³ has pointed out, is completely at variance with the data obtained from careful studies of the rearrangements of the picryl ethers and the benzene sulphonyl esters of ketoximes⁴. Secondly, Brodsky and Micluchin⁵ in some recently available publications, have questioned the correctness of the usually accepted view of the intramolecular nature of the transformation because the benzamide formed by the addition of water, containing an excess of the heavy isotope O^{18} , to the product resulting from the rearrangement of benzophenone oxime by phosphorus pentachloride itself contained O^{18} .

In any formulation of the mechanism of the Beckmann rearrangement, it has to be remembered that the change involves the migration of two radicals: (a) the hydrocarbon radical R from carbon to nitrogen, and (b) the OH or OX group from nitrogen to carbon. Campbell and Kenyon's elegant demonstration⁶ that the product resulting from the rearrangement of the oxime of (+)- α -phenylethylketone, in which the migrating group is linked to the rest of the molecule by an asymmetric carbon atom, possesses 99.6 per cent of the activity of optically pure (-)-aceto- α -phenylethylamine relates to process (a) only, but it proves conclusively that the asymmetric migrating group is never kinetically free: electron-sharing between it and the remainder of the molecule must be continuous throughout the rearrangement. With regard to process (b), there is as yet no clear-cut evidence as to the mode of transit of OX from nitrogen to carbon; this may occur by an intramolecular route or by dissociation into free ions. Although the data are well interpreted by an intramolecular migration, there is in the picryl ethers and benzene sulphonyl esters no reason to object to the mechanism:

nor for the rearrangement by an acid reagent to

Indeed, Chapman⁷ has found that when a mixture of the homopicyl (that is, 2:4:6-trinitro-*m*-cresyl) ether of benzophenone oxime and the picryl ether of di-*p*-tolylketone undergoes rearrangement on heating the product contains some *p*-toluoyl-*N*-homopicyl-

p-toluidide, $p\text{-Me.C}_6\text{H}_4\text{CO.N} \begin{cases} \text{C}_6\text{H}(\text{NO}_2)_3\text{Me} \\ \text{C}_6\text{H}_4\text{Me}(p) \end{cases}$ This may arise as the

result of the ionization of OX^+ but, on the other hand, it may conceivably be the consequence of exchange in the picryl ethers before rearrangement.

If, however, ionization occurs, it must either occur simultaneously with, or after migration of, the group R . It cannot precede it, otherwise there would not be such a strict stereochemical determination of the products in rearrangements of this kind.

The new evidence of Brodsky and Micluchin, based on the use of the isotope O^{18} , from which it is concluded that the rearrangement is not intramolecular, is open to criticism because of the use of phosphorus pentachloride. Although its function in the Beckmann rearrangement has never been fully worked out, its action on the oxime is presumably similar to that on other hydroxy compounds, namely:

If this be so, then its role in the rearrangement of a ketoxime may be formulated as follows:

Compound (V) on decomposition can give rise to an oxygen-free compound (VI), which will inevitably yield with water enriched with the heavy isotope O^{18} an amide (VIII) containing O^{18} . It is therefore clear that although process (b) may well prove in fact to be an intermolecular process, the new data of Brodsky and Micluchin do not by themselves disprove an intramolecular mechanism of the transformation.

From the combined data at present available, it may be concluded that the Beckmann change involves: (a) an intramolecular migration of the hydrocarbon radical R from carbon to nitrogen, and (b) a simultaneous or subsequent transfer of the group OX to the carbon atom (with the eventual formation of the amide) which is possibly intermolecular in character.

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¹ Higman, *Nature*, **156**, 242 (1945).

² LeFevre, *J. Soc. Chem. Ind.*, **49**, 391 (1945).

³ Dewar, *Nature*, **156**, 688 (1945).

⁴ For summary and references, see Brynmor Jones, *Chem. Rev.*, **35**, 335 (1945).

⁵ Brodsky and Micluchin, *C.R. Acad. Sci. U.S.S.R.*, **32**, 558 (1941). *J. Chem. Phys.*, **11**, 342 (1943).

⁶ Campbell and Kenyon, *J. Soc. Chem. Ind.*, **49**, 391 (1945), and private communication.

⁷ Chapman, private communication.