

the meta hydrogens might account for the latter high value. Using the average value of  $k_D = 1.2$  (uncorrected) and the values for the over-all  $k_T$ 's observed in experiments 2 and 5, the partition ratio for T and D is calculated to be approximately 1.2. The corresponding calculation for the  $k$  of T and H is very sensitive to experimental error; a value of approximately 2.0 is obtained, which seems very high. The apparent confirmation of this latter value by the results of experiments 8, 9 and 12 with benzidine is very probably fortuitous. The assumption that  $k = 1.00$  for the exchange of T with amino H's is obviously questionable.

The triterated crystal violet lost only about 2% of its T-activity on standing in 2% aqueous solution for three months at room temperature. Heating this solution for seven days at 100°, with added sulfuric acid catalyst, caused a loss of 60% of the activity. The deuterated methylene blue (expt. 4) was heated with 1 cc. of water at 100° for two hours with no acid catalyst present. The calculated  $\Delta d$  for exchange of the 3H<sub>2</sub>O of crystallization only was 0.0104, actually observed 0.0111. Such exchange was incomplete in only five minutes of heating or in twenty-four hours at room temperature.

As noted above, the values given for benzidine may not be valid. The calculated effect is a small one derived from the large observed effect due chiefly to exchange of the four amino H's. However, one interesting feature of the  $k$  values can be noted; that is, the very low values of the partition ratios in general. That these are real and not merely an indication of a slow rate of reaction is indicated first in experiment 10. Here, increased solubility was achieved by using a 50% aqueous ethyl alcohol mixture as the exchange medium. This is further substantiated by experiment 11. According to the theory and actual observations of Ingold, *et al.*,<sup>1</sup> on the exchange of phenol, and of Brown, *et al.*,<sup>9</sup> on dimethylaniline, the conditions in expt. 11 are such as to yield the maximum possible rate of exchange. The result of expt. 12 as compared to expt. 9 is also consistent with the latter theory. The lower partition ratio observed in the aqueous alcohol mixtures can be explained in part by the observation of Kharasch, Brown, *et al.*,<sup>2,8</sup> that  $k_D$  in pure ethyl alcohol as exchange medium is about 0.85 (as compared to approxi-

mately unity in water). The low value of  $k$  observed with benzidine seems to be in accordance with the theory of exchange activation by appearance of a negative charge on the ortho and para positions through the quinoidal resonance forms (of the free base in the case of aromatic amines). For in the case of benzidine there must be an interference between the resonances of the two groups with the aromatic nucleus, since the two resonance systems induce similar charges in the benzene rings. Such an effect does not seem to appear in the results obtained by Brown and Letang<sup>10</sup> with various dimethylamino-naphthalene derivatives.

A similar resonance interaction would account for the relatively small exchange observed with the symmetrical dyestuff congo red. Accordingly, it was also ascertained that under the conditions employed herein, little or no exchange occurred in the dyes trypan blue and trypan red. Other effects may also be operating here, including the steric hindrance of resonance ("peri-effect") observed in naphthalene derivatives.<sup>9</sup>

**Acknowledgment.**—The author gratefully acknowledges the interest and advice of numerous members of both the Radiation Laboratory and the Department of Chemistry. This work was supported by funds from the A. B. Miller Foundation.

(10) W. G. Brown and N. J. Letang, *ibid.*, **63**, 358 (1941).

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## X-Ray and Optic Measurements on $\beta$ -Lactoglobulin

BY I. FANKUCHEN

Through the courtesy of Dr. T. L. McMeekin, a large air-dried crystal of  $\beta$ -lactoglobulin was made available to the writer. In the only published work on this material,<sup>1</sup> no optic data (save the sign of the birefringence) and no correlation of the crystallographic axes with the physical directions of the crystal were given. It was thought desirable in view of McMeekin and Warner's<sup>2</sup> observations on shrinkage to make these measurements.

The crystals are of the orthorhombic variety designated by Crowfoot as tabular. The small-

(1) D. Crowfoot, *Chem. Rev.*, **23**, 215 (1941).

(2) T. L. McMeekin and R. C. Warner, *THIS JOURNAL*, **64**, 2393 (1942).

(9) W. G. Brown, A. H. Widiger and N. J. Letang, *THIS JOURNAL*, **61**, 2597 (1939).

est refractive index,  $\alpha$ , lies in the main prism face at right angles to the prism length. The other two vibration directions  $\beta$  and  $\gamma$  are parallel to the thickness and length of the crystal but could not be identified as the crystal is almost uniaxial. This agrees with Crowfoot's determination of the sign of the birefringence as negative.

The "c" axis was found to be 111 Å. and corresponds in direction to  $\alpha$ , the crystal width. The crystal length, "a," is 60 Å. and the thickness "b" is 62 Å. These values agree very well with Crowfoot's cell values 110, 60 and 63 Å., respectively. This identifies the material as the lactoglobulin that Crowfoot studied, and, therefore, her unit cell measurements 154, 67.5 and 67.5 for the wet crystals can be used to determine cell shrinkage in the various crystal directions. The agreement between these shrinkages and those observed by McMeekin and Warner on the actual crystal is very good. It is also interesting to note that the approximate uniaxial optic character of the crystal agrees with the approximate tetragonal shape of the unit cell. This may, of course, be only a coincidence and have no bearing on any characteristics of the molecular arrangement.

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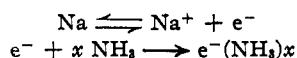
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## The Hydrogenation of Disubstituted Acetylenes

BY KENNETH W. GREENLEE AND W. CONARD FERNELIUS

Campbell and Eby<sup>1</sup> have recently shown that the treatment of dialkylacetylenes with sodium in liquid ammonia produces the pure *trans* forms of the corresponding olefins. These investigators offer no explanation for this startling phenomenon. The following suggested mechanism seems to account satisfactorily for the observed results.

A solution of sodium in liquid ammonia contains electron ions<sup>2</sup>

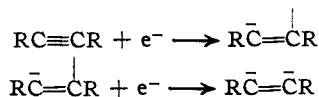


The reaction of sodium with double and triple bonds consists in the addition of electrons<sup>3</sup>

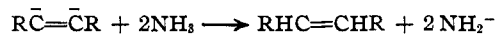
(1) K. N. Campbell and L. T. Eby, *THIS JOURNAL*, **63**, 216-219 (1941).

(2) For references see W. C. Fernelius and G. W. Watt, *Chem. Reviews*, **20**, 195-258 (1937).

(3) For a review of reactions of solutions of metals see Fernelius and Watt, ref. 2.



followed by partial or complete ammonolysis



In the ionic intermediate, the electrons would repel each other into positions as far apart as possible, *i. e.*, the *trans* form. The configuration once fixed in the ion (either before or after the addition of the second electron), persists in the ammonolysis (or hydrolysis) product. The pic-

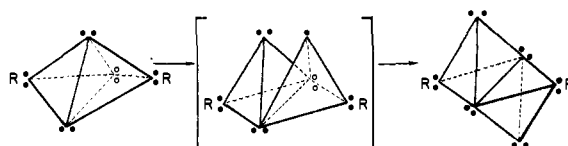


Fig. 1.

ture of one of the carbon tetrahedra turning inside out like the frame of an umbrella is the same mechanism as that frequently offered for the Walden inversion.<sup>4</sup>

(4) W. A. Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1936, pp. 331-336.

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## The Nitration of 4-Phenylphenyl Benzoate

BY STEWART E. HAZLET AND HARRIS O. VAN ORDEN

Earlier studies on the bromination of esters containing diphenyl groups, including the bromination of 4-phenylphenyl benzoate,<sup>1</sup> have been reported from this Laboratory.<sup>2</sup> In the work here reported an attempt was made to compare the nitration of an ester with the bromination of the same compound. Methods of investigation were essentially the same as in previously reported work.<sup>2</sup> For reference compounds, the nitrophenylphenols were prepared by methods on record, and the corresponding benzoates were prepared by the action of benzoyl chloride on the nitrophenols.

Nitration of 4-phenylphenyl benzoate was effected under conditions somewhat similar to those employed in the bromination which was reported earlier,<sup>1</sup> and 4-(4-nitrophenyl)-phenyl benzoate resulted. The course of this nitration, then, is strictly parallel to the analogous bromination.

(1) Hazlet, Alliger and Tiede, *THIS JOURNAL*, **61**, 1447 (1939).

(2) Cf. Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942), for the last paper in this series.