prepared in the three alcohols, and also (with greater difficulty) in aqueous alkali. On extracting alkali from the filaments with absolute methanol, the fiber pattern disappears, and is not restored by humidification. Soaking in 75% alcohol containing 2% alkali restores the original pattern, whereas 75% alcohol alone produces the V structure. The fiber pattern (Fig. 1) can be indexed on the basis of an orthorhombic unit cell having $a_0 = 9.0$ Å., $b_0 = 22.7$ Å. and $c_0 = 12.7$ Å. and containing twelve $C_6H_{10}O_5\cdot(KOH)_x$ groups. x has not been established and may be variable, since the alkali uptake of the fibers giving this pattern depends on the alkali concentration in the deacetylating medium. Lithium, sodium and cesium hydroxide amylose have similar structure and composition.

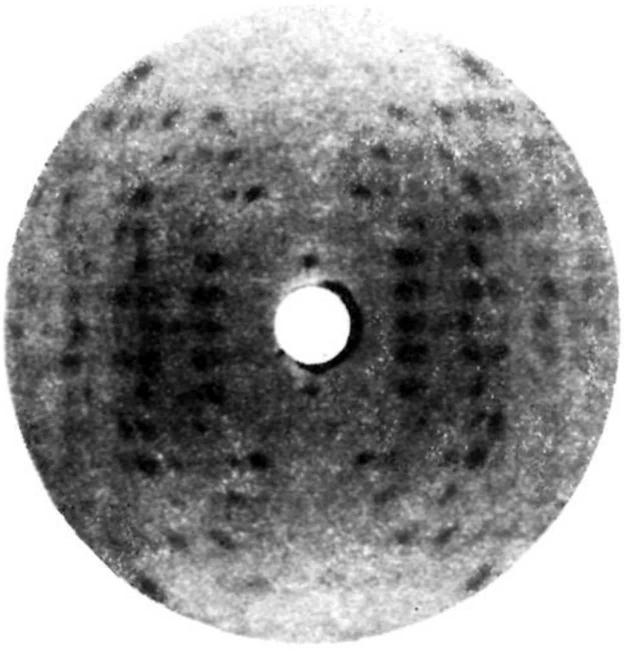

Fig. 1.—Fiber diagram of potassium hydroxide amylose. Fiber axis vertical, filtered Cu radiation, 5 cm. distance.

Transformation of the alkali amylose structure to the V structure is effected most easily in 75% methanol, allowing the clamped filaments to contract 10 to 15%. The diffraction pattern is independent of the primary alcohol and shows a fiber repeat period of 8 Å. Lateral spacings vary with moisture content. Extraction of alkali with 75% *t*-butanol results in a fiber pattern with similar fiber period, 7.9 Å., but lateral reflections are considerably shifted and indicate a monoclinic unit cell.

Filaments giving fiber patterns that correspond to the A (cereal starch) structure are obtained by exposing alkali amylose to high humidity (80%) for several days. The fiber identity period is 10.5 Å., at variance with the unit cell proposed[2] from powder patterns.

In saturated water vapor the A structure changes to the B (tuber starch) structure. Complete conversion and sharpest fiber patterns result from boiling vapor-treated filaments in water.

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[2] Bear and French, THIS JOURNAL, **63**, 2298 (1941).

THE STRUCTURE OF KETENE

Sir:

In a recent paper Hannay and Smyth[1] have found ketene to possess a dipole moment considerably less than those of aldehydes and ketones and have concluded that "the oxygen has much less negative charge than the ordinary carbonyl oxygen." This fact they explain in terms of four resonance structures.

In two papers[2,3] the printing of one of which has been greatly delayed owing to post-war difficulties in this country, we have been able—mainly from a study of the ionization potentials of the non-bonding electrons on the oxygen atoms—to arrange a long series of carbonyl molecules in the order of increasing C=O bond polarity. As a result it has become clear that as the polarity increases so the bond weakens, that is, the stretching force constant and bond energy decrease and the bond length increases. It is therefore not satisfactory to describe the polarity of a carbonyl bond in terms of covalent–ionic resonance, for such a description would imply an *increase* of bond strength with increasing bond polarity (up to 50% ionic character) and a greater strength in the polar than in the non-polar bond.

Our work showed that ketene had a C=O bond polarity considerably less than that of the aldehydes, with which fact the work of Hannay and Smyth is in accord. A simple and satisfactory explanation is possible without recourse to the postulation of resonance forms. It is essential to realize that the central carbon atom in ketene is really an "acetylenic" or "digonal" one, that is, it is forming two hybrid *s–p* bonds at 180° and two π bonds. The two π bonds have their central planes at right angles, so that conjugation does not occur between them. Now a carbon atom exerting a hybrid valency has a stronger electronegativity the greater the proportion of *s* character in that valency. In other words a carbon atom of a CH bond exerts a greater "pull" on those CH electrons if the carbon is part of a triple than of a single C–C bond. This statement may either be regarded as a strongly founded theoretical conclusion[4] or as a simple deduction from such experimental facts as the acidity of acetylene. It is therefore clear that the C=O bond in ketene will have considerably reduced C^+O^- polarity relative to formaldehyde. The other properties of ketene (for example, low carbonyl bond length, high carbonyl bond stretching force constant, high carbonyl bond energy, all relative to aldehydes and ketones) then follow from this reduced carbonyl polarity.[3]

Carbon dioxide is another example of a molecule containing a "digonal" carbon atom. In this case the competition of the two C=O bonds is a further factor reducing the bond polarity. Ac-

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[1] Hannay and Smyth, THIS JOURNAL, **68**, 1357 (1946).
[2] Walsh, *Trans. Faraday Soc.*, **42**, 56 (1946).
[3] Walsh, *ibid.*, in press.
[4] Coulson, private communication.

cordingly, carbon dioxide has a carbonyl bond polarity much smaller than that of ketene. Again the cumbrous resonance description is neither necessary nor desirable. The organic isocyanates of course occupy an intermediate position. Carbon suboxide, with all its carbon atoms in the "digonal" state must have a carbonyl bond polarity close to that of ketene. Accordingly its chemical properties resemble those of ketene.

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NEW BOOKS

Physical Methods of Organic Chemistry. Vol. II.[1] ARNOLD WEISSBERGER, Editor. Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y., 1946. vii + 631 pp. 23 1/2 × 15 cm. Price, $8.50.

With this second volume, the editor has completed a work which will be of considerable value to organic chemists. The subjects covered in it are as follows: XVII, Spectroscopy and Spectrophotometry; XVIII, Colorimetry, Photometric Analysis and Fluorimetry; XIX, Polarimetry; XX, Determination of Dipole Moments; XXI, Conductometry; XXII, Potentiometry; XXIII, Polarography; XXIV, Determination of Magnetic Susceptibility; XXV, Determination of Radioactivity; XXVI, Mass Spectrometry.

The quality and value of the several chapters varies greatly. The chapter on polarimetry is quite complete and appears to the reviewer to be the best modern monograph on the subject. The chapter on dipole moments is the shortest in the book (22 pages) and is hardly more than a qualitative description of a method of determining the dipole moment.

The chapter on the measurement of radioactivity is good as far as it goes. The discussion of the measurement of soft beta rays, however, is definitely inadequate in view of the fact that the most important activities for organic chemists, namely, C^{14} and H^3 are both very soft beta emitters. It is almost certain that special treatises on this subject will appear soon.

For most of the subjects discussed in this volume there already exist quite complete monographs.

The general impression one gets on reading this volume is one of pleasure and interest in the unfamiliar subjects and disappointment in the familiar ones. This would seem to indicate that the book will only partially fulfill its purpose of "... relieving him (the chemist) of much of this burden ... to search through periodicals and specialized books."

It is undoubtedly a valuable book to have on ones desk primarily for the purpose of becoming generally familiar with a heretofore unfamiliar physical method, but for actual laboratory use it will still be necessary, in most cases, to go to the specialized literature which is quite amply documented in this book.

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(1) Vol. I is reviewed in THIS JOURNAL, **67**, 2278 (1945).

MELVIN CALVIN

Semi-Micro Quantitative Organic Analysis. By R. BELCHER, F.R.I.C., Scientific Officer, British Coke Research Association, and A. L. GODBERT, M.Sc., Ph.D., Scientific Officer, Safety in Mines Research Board. Longmans, Green and Co., Inc., 55 Fifth Avenue, New York, N. Y., 1946. viii + 168 pp. 42 figs. 14.5 × 23 cm. Price, $3.00.

The book presents in orderly fashion quantitative semimicro methods for the determination of the more common elements and groups, as well as molecular weights of organic compounds. The chapters on the various analyses are preceded by a rather thorough treatment of the ordinary analytical balance. Thus detailed directions for assembling, dismantling, cleaning and testing are given as well as procedures for the determination of its sensitivity and precision and the calibration of weights. The "swing method" of weighing is utilized and for the average sample size of 20 milligrams employed throughout, a balance with a precision "not worse than 0.04 mg." is recommended.

The analytical methods are followed by description of a few physical tests (determination of density, melting and boiling points (Mulliken, Emich and Siwoloboff methods)). This is followed by appendices containing procedures for the purification of small amounts of organic solids and liquids and directions for the preparation and standardization of the various standard solutions used (0.025 *N* hydrochloric acid, sodium hydroxide, barium chloride, potassium dichromate, ferrous ammonium sulfate, sodium thiosulfate and 0.05 and 0.02 *N* silver nitrate solutions). In addition to this, the book contains a list of 46 references and a short index.

The determination of carbon and hydrogen, for which an accuracy of ±0.2% is claimed and which is one of the few gravimetric methods (the others being the determination of residues and of phosphorus) presented, employs the principle of removable combustion tube fillings. The apparatus dispenses with the usual bubble counter, but employs a suitable flow-meter instead. With the exception of the larger combustion tube (57 cm. length instead of 52 cm. and 1-1.2 cm. diameter, instead of 0.8 cm.) the rest of the apparatus, as well as the procedure, is exactly the same as in the corresponding micro-method. The removable combustion tube filling consists of a platinum wire gauze, a mixture of copper oxide, lead chromate and ceric oxide wrapped in copper gauze and lead super oxide contained in a porcelain boat. The latter is good for about 15 combustions. The combustion boat is placed between the two metal gauzes. Combustion is carried out in an atmosphere of oxygen only. The absorption tubes, the construction and the filling of which are again exactly the same as in the conventional micro method, are weighed without replacement of the oxygen by air.

The determination of nitrogen, gasometric (Dumas) as well as volumetric (Kjeldahl) procedures are available, patterned after the corresponding micro methods. The nitrometer is graduated up to 8 ml. with subdivisions into 0.02 ml. instead of the usual 1.5 ml. with 0.01 ml. subdivisions. For the volumetric determination of sulfur and the halogens (chlorine, bromine and iodine) the dry combustion method is employed. The accuracy claimed for all these determinations is again ±0.2%.

In the structure analytical methods, for which accuracies varying from ±0.3% (methoxyl) to ±0.5% (carboxyl and acetyl) are claimed, no new principles are employed, while in the chapter dealing with the determination of molecular weights, the methods of Sucharda-Bobranski (ebullioscopic), Rast (cryoscopic) and Bratton and Lochte (vaporimetric), with accuracies of ±5%, are given.

The book, the individual chapters of which follow the by now well acclaimed arrangement of subdivision into principle, apparatus, reagents, method and calculation, is primarily intended for teaching purposes. It appears, however, that the volumetric methods might well lend