(i) The longest wave length maxima for the benzo compounds lie appreciably further toward the red than do those of the corresponding monocyclic derivatives (Table I). This is attributable to the far greater number of dipolar structures in the benzo series. While contributions from dipolar structures stabilize both ground and excited states in both series, their more significant contribution in the excited states is reflected in over-all decrease in excitation energy in the benzo series as compared to the monocyclic series.

(ii) The differences in excitation energies between the α- and γ-compounds are very much smaller in the benzo series (Table I). This results from the somewhat decreased relative importance of the dipolar naphthalenoid structures (C_{3-5} and D_{3-5}) in the benzo series. The greater spread of the integrated intensity values within both the α- and γ-groups of the benzo series as well as the substantial deviations of the intensity ratios from the r^2 ratios presumably is a consequence of the same circumstance. The anomalously low intensity of 3-methyl-4-quinolone (VIe) may be due to steric hindrance between the methyl and carbonyl groups.

(iii) All of the benzo compounds show either maxima or well-defined plateaus at wave lengths below the principal maxima, while the monocyclic compounds show only one band in the conventionally accessible region of the spectrum. The following explanation for this is in terms of the γ-compounds but applies equally well to the α-compounds. In the monocyclic series, we may represent the ground state energy essentially by that of A_1, slightly depressed by resonance contributions from the dipolar structures. The degenerate first-approximation excited state, made up largely of the energetically equivalent structures A_2 and A_3 is split by resonance into two-widely separated energy levels. Transition from the ground state to the lower of these two levels accounts for the observed single band, while transition to the higher level is presumably outside the range of the conventional instruments. In the benzo series, however, the first-approximation ground and excited states are both highly degenerate and markedly split by resonance, the ground state into two levels, principally by interaction between the benzenoid structures D_1 and D_2 and the excited state into three levels, principally by interaction among the naphthalenoid structures D_{3-5}. It seems probable that the upper level derived from the original ground state and the lower level derived from the original excited state will be sufficiently close together in energy so that significant further interaction will occur. The magnitude of the resultant resonance splitting will depend on the proximity of the levels. If these are only moderately close together, as seems reasonable, the split will be comparatively small and there will be two low-lying excited states with only a comparatively small difference in energy between them.[8] This energy difference should be roughly comparable throughout the benzo series, an expectation in good agreement with experiment. The average spacing for the eight members of the series is 16 ± 2 kcal./mole.

Acknowledgment.—The author is indebted to Dr. Verner Schomaker for stimulating comments and suggestions.

[8] A further approximation would take into account an additional perturbation of the second excited state by interaction with the next higher state. If the energy relationships are similar in magnitude to those in our discussion above, the third excited state level might be experimentally observable. Indeed, this is found as a maximum in the region 230–240 mμ (not indicated in the table) in the spectra of all the nitrogen compounds of the benzo series (Vb, Vc, VIb, VIc, VId, VIe).

LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XVIII. A New Type of Reactor and the Mild Fluorination of Carbon Disulfide[1]

BY EDWARD A. TYCZKOWSKI[2] AND LUCIUS A. BIGELOW

RECEIVED FEBRUARY 6, 1953

A new type of metal packed direct fluorination reactor incorporating a concentric tube burner designed from a study of fluorine diffusion flames has been built and operated. It has been shown by direct comparison to produce a very mild fluorination reaction in which both cleavage and polymerization appear to be reduced. The new reactor has been applied to the mild fluorination of carbon disulfide which has resulted in the isolation of the new and interesting perfluoro compound $SF_5CF_2SF_5$. This was accompanied by the new $SF_3CF_2SF_5$ and CF_3SF_3, as well as an unusually pure sample of S_2F_{10}, and a variety of additional cleavage products.

This paper describes the construction and operation of a novel design of fluorination reactor; and is also the second[3] of a group which will deal with the vapor phase fluorination, largely under mild conditions, of typical organic compounds containing nitrogen or sulfur.

In this Laboratory careful studies have been made of the performance of a considerable series of metal packed fluorination reactors, the efficiencies of which have increased with our experience; but nevertheless relatively little knowledge has been gained as to what actually takes place within such a unit. The last of these was the T-reactor, designed by Gilbert,[4] in which the sample on carrier

---

[1] This paper was presented at the September, 1952, Meeting of the American Chemical Society in Atlantic City; and has been constructed from portions of the Doctorate Thesis to be offered by Edward A. Tyczkowski to Duke University in the Spring of 1953.

[2] Allied Chemical and Dye Corporation Fellow, 1950–1951; Atomic Energy Commission Fellow, 1951–1952.

[3] See J. A. Cuculo and L. A. Bigelow, THIS JOURNAL, **74**, 710 (1952).

[4] A. R. Gilbert and L. A. Bigelow, *ibid.*, **72**, 2411 (1950).

nitrogen on the one hand and diluted fluorine on the other entered through the opposite side-arms, respectively. Here they were dispersed over a metal packing and later passed inward and downward through the body of the unit to react over the metal surface. This arrangement proved very efficient for the fluorination of highly deactivated samples, but was much less satisfactory when reactive materials were used. At this point it was decided to construct and operate a glass model of this type to see what was actually taking place, after which the packing was carefully examined to determine how well the reaction had been dispersed. It was found that even after the volume rate of flow of the reactants had been equalized by adjusting the diluent nitrogen, the high velocity reaction had taken place almost entirely in a thin perpendicular plane down through the center of the reactor, leaving the greater part of the packing unaffected. Also the fluorination gave off a continuous glow, easily seen in the dark, which appeared to behave very much like a flat diffusion flame.

These basic observations led to a study of fluorine diffusion flames and this through many preliminary experiments finally resulted in the design of the concentric tube burner illustrated to scale in Fig. 1.

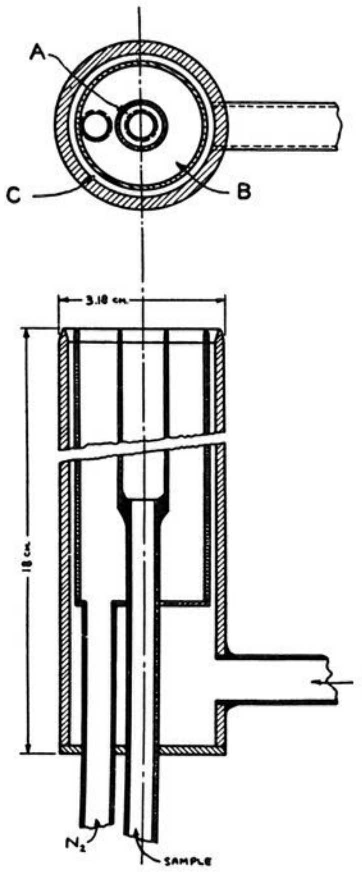


Fig. 1.—Concentric tube burner.

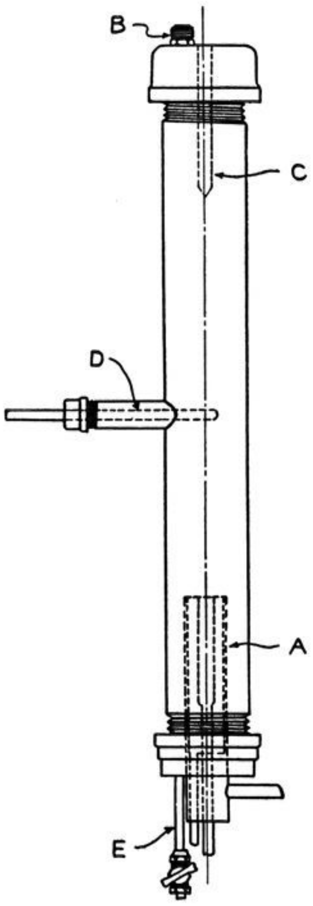


Fig. 2.—Flame reactor.

Here the sample entered on carrier nitrogen through the center tube, and undiluted fluorine through the outer ring, while diluent nitrogen was admitted as a barrier between them, thus permitting the reactants to diffuse into each other more gradually. When this burner was operated at the base of a large glass tube, it was possible to produce at will a small hot luminous flame, a taller blue conical flame, or at higher dilutions the latter could be blown out into a much taller faintly glowing column of reacting gases which appeared to represent a very mild type of fluorine combustion.

Then this burner was incorporated into the base of the vertical cylindrical unheated metal reactor as shown in Fig. 2, and this was packed with copper shot. When such a reactor was operated under conditions corresponding to those producing the mildest reaction in the glass tube, it was found that the reaction had been spread out over the surface of the metal packing far better than before. Strictly comparative runs were then made using the old and new reactors, respectively, and the results revealed beyond doubt that with the new burner both cleavage and polymerization were markedly reduced, while the formation of simple fluorinated products was strongly favored; all of which indicated clearly that a considerably milder form of direct fluorination had been taking place than had been obtainable heretofore with chemically reactive samples.

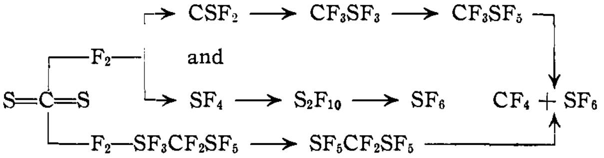
Therefore, it was decided to undertake the very mild fluorination of the technically important solvent carbon disulfide, with the hope of preparing among other things the hitherto unknown perfluoro compound $SF_5CF_2SF_5$ without cleavage. Accordingly, the carbon disulfide was carried on nitrogen from a special low temperature glass saturator into the new reactor and fluorinated at the molar reaction ratio of 5:1:75, and the relatively low average temperature of 48°. Since hydrogen fluoride had been removed from the incoming fluorine, this compound could not have been present in the reaction mixture. The crude product after mechanical separation from some unchanged sample turned out to be a complex and highly reactive mixture which has been fairly well resolved into its components by repeated rectifications at both elevated and reduced pressures, together with a number of low temperature crystallizations and filtrations. There were finally isolated in the order of their boiling points CF_4, SF_6, CSF_2, SF_4, CF_3SF_5, CF_3SF_3 (b.p. −7°, f.p. −110°), S_2F_{10} (b.p. 25°, f.p. −72°), $SF_3CF_2SF_5$ (b.p. 26°, f.p. −51°), and the desired $SF_5CF_2SF_5$ (b.p. 62°, f.p. −70°). Of these the $SF_5CF_2SF_5$, $SF_3CF_2SF_5$ and CF_3SF_3 were entirely new. The $SF_5CF_2SF_5$ and S_2F_{10} were obtained in highest analytical purity, while the $SF_3CF_2SF_5$ and CF_3SF_3 were nearly so. The freezing curves throughout had adequate reproducible plateaus, and there was no reason to doubt the presence of all of the compounds listed in the product in significant amounts with the possible exception of the CSF_2. The interesting perfluoro compound $SF_5CF_2SF_5$ and also the related $SF_3CF_2SF_5$ froze to highly crystalline white solids and were unaffected by heating with dilute alkali solutions. The former compound represents the first known case in which two $—SF_5$ groups are linked into a single organic molecule. The S_2F_{10} had a melting point twenty degrees higher than the commonly accepted value previously reported,[5] and is known to be moderately reactive and quite toxic. On the other hand, the CF_3SF_3, CSF_2 and SF_4 were extremely reactive, and underwent very rapid hydrolysis in the presence of water or bases.

Although there are still a number of points in

---

(5) K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

this fluorination which remain to be resolved, it is nevertheless felt that these results give quite a clear picture of the chemistry involved in the mild direct fluorination of carbon disulfide. They may also be illustrated by the following representative scheme, although this atomic fluorination obviously could and probably did follow a number of different routes simultaneously.



Further uses for the new reactor, which appears to produce the mildest direct fluorination yet described, and also the problem of fluorine diffusion flames, are now under active investigation.

Experimental

The Concentric Tube Burner Reactor.—The burner (Fig. 1) was constructed from three brass tubes placed within each other; the inner one, i.d. 0.87 cm., o.d. 0.95 cm., being 11 cm. long; the middle one, i.d. 2.40 cm., o.d. 2.56 cm., 15 cm. long; and the outer one, i.d. 2.85 cm., o.d. 3.18 cm., 18 cm. in length. The lower ends of the two outer tubes were covered by brass plates silver soldered on; and two copper $^1/_4''$ o.d.-inlet tubes passed directly up through them leading to the central tube A and the middle annular space B, while a third $^3/_8''$ o.d. inlet at the right supplied the outer annular space C. The open ends of the burner tubes were tapered to sharp edges to provide for stream line flow of the gases; while the arrangement shown in the figure served also to hold them firmly in position.

The main body of the reactor (Fig. 2) was constructed from a 56-cm. length of 2.5″ i.d. brass pipe closed at both ends by iron pipe caps with lead seals. The top cap carried a well C, for a Weston thermometer and a $^3/_8''$ flare fitting B, to which the exit tube was attached. The bottom cap carried the burner A, which extended 13 cm. into the reactor body, and a small stainless steel needle valve E, to serve as a drain. Halfway up the reactor a 6 cm. length of $^1/_2''$ i.d. brass pipe was welded on and fitted with a leaded cap containing a well for a glass thermometer. A Weston thermometer could not be used because it could not be inserted to the proper depth. The entire reactor was then packed with copper shot including the upper portions of the burner tubes; but the lower parts of these as well as the extreme top of the reactor were filled with copper wool in order to avoid obstruction of either the inlet or exit lines by pieces of metal.

In operation, the reactor was first fluorinated thoroughly to remove organic matter and form a fluoride surface on the metal. Then it was flushed with nitrogen, after which the reactants and diluent were admitted essentially at the same time.

Comparison of the Old and New Reactors.—About this time Mr. W. W. Leake of this Laboratory was carrying out the fluorination of propionitrile in the T-reactor, and kindly agreed to repeat one of his runs under identical conditions, using the new burner type reactor for purposes of strict comparison. Accordingly C_2H_5CN was fluorinated at a molar reaction ratio of 7:1:21 and average temperature of 80°, after which the product was condensed, stabilized and rectified exactly as before. The comparative results, expressed as volume per cent. conversion, are summarized as follows, where the figures in parentheses represent the products from the older T-type reactor: $CF_4 + C_2F_6 +$ transition 9 (29); C_3F_8 47 (54); $CF_3CF_2CHF_2$, b.p. 17°, 44 (12); transition 8 (6); b.p. near 0° 5 (3); higher and residue 14 (18). This indicates decreased cleavage and polymerization, but increased fluorination to simple molecules, especially the intermediate $CF_3CF_2CHF_2$, in the new reactor as compared with the old.

The Fluorination of Carbon Disulfide.—The carbon disulfide (reagent grade, 97 cc. in all), diluted with 6.13 l. of nitrogen per hour, was carried from a special glass bubble type saturator, with an integral spray trap filled with glass beads, maintained at 0° by an ice-bath, at the rate of 0.05 mole (3.8 g.) per hour into the central tube of the unheated burner, above which, within the meshes of the packing, it met and reacted with 0.25 mole (9.5 g.) per hour of undiluted fluorine (free from HF), which was admitted simultaneously into the outer ring of the burner. At the same time 86 l. per hour of barrier diluent nitrogen was admitted through the middle ring, with the result that the sample was fluorinated at the molar reaction ratio (F_2:sample:N_2) of 5:1:75, corresponding to a fluorination ratio of 5:1 and a dilution ratio of 1:15, at an average equilibrium temperature of 48° (middle 52°, top 44°). The exit gases were condensed in a series of 300 × 58 mm. glass traps using 4 mm. stopcocks, the first cooled by CO_2–acetone and the others by liquid air. After 32 hours of operation, 191 cc. of total crude product containing no HF had been collected, which was heterogeneous (top layer 15 cc.). First the CF_4 present was distilled off, after which the product was liquefied and the upper layer, later shown to contain only CS_2, removed mechanically. Then the entire fluorinated product, 176 cc., was recombined and carefully rectified, partly at elevated pressures in order to distil the SF_6, and later at reduced pressures, with the results as shown in detail in the following Table I.

TABLE I

THE RECTIFICATION OF FLUORINATED CARBON DISULFIDE

Reaction ratio 5:1:75; av. temp., 48°; total vol., 176 cc.

Fraction	B.p., °C.	Mol. wt. (obsd.)	Liq. vol. % of total product
CF_4	−130	88	11
SF_6	−54 (2.3 atm.)	133–143	20
3	−35 to −27 (2 atm.)	114	9
4	−27 (2 atm.)	130	18
5	−26 (2 atm.)	112	10
6	−8	131	9
7	−5	153	2
8	−7 to −5 (200 mm.)	256–282	11
9	21 (156 mm.)	314–336	3
Transitions	....	.....	7
Residue and loss	....	.....	2

At the end of fraction 8, the product began to attack the glass of the still. It was removed, stabilized by refluxing with 5% NaOH, dried, and the fractionation resumed with a loss of only 1.5 cc.

Fraction 3.—This highly reactive mixture (16 cc.) of at least three components was partially frozen at −110 to −120°, and filtered through a filter stick yielding a residue (6 cc.) and a filtrate (10 cc.). The former, on fractionation, finally yielded pure CF_3SF_5 (1 cc.), b.p. −21°, mol. wt., 198 (known[6] b.p. −20.4°, mol. wt., calcd., 196). The latter similarly gave not quite pure CSF_2 (1.5 cc.), b.p. −46°, f.p. −134°, mol. wt., 90 (known[7] but not certain, b.p. −40°, f.p. −136°, mol. wt. calcd., 82). All the evidence indicates that fraction 3 contained CF_3SF_5 and probably some CSF_2, presumably contaminated by SF_4 and possibly the little known SF_2 (mol. wt., 70) and even SiF_4 from the glass.

Fractions 4 and 5.—These portions were highly reactive and corrosive mixtures which resisted all efforts at complete separation. They appeared to contain considerable amounts of substances with both higher and lower molecular weights than the main body of the material, and may have been highly contaminated by SiF_4 from the glass as well. However after repeated partial crystallizations at low temperatures, followed by many rectifications of both residues and filtrates, numerous fractions appeared with similar characteristics, some of which on combination and further fractionation yielded not entirely pure SF_4 (5 cc.), b.p. −38°, f.p. −122°, mol. wt., 109 (known[8] b.p. −40°, f.p. −124°,

---

(6) G. A. Silvey and G. H. Cady, THIS JOURNAL, **72**, 3624 (1950).

(7) W. Kwasnik and P. Scherer, "Recent German Research Work on Fluorine and Fluorine Compounds," U. S. Department of Commerce, Washington, D. C., 1947, p. 10, 26.

(8) J. Fischer and W. Jaenckner, *Z. angew. Chem.*, **42**, 810 (1929).

mol. wt. calcd., 108). The freezing curve had a good plateau at −122°, but some solid began to separate at −100°. It was concluded that fractions 4 and 5 were inseparable constant boiling mixtures, not necessarily azeotropic, presumably consisting largely of SF_4 (mol. wt., 108), but probably containing considerable amounts of CSF_2 (mol. wt., 82), together with some material of high molecular weight, and quite possibly SiF_4 (mol. wt., 104) as well.

Fractions 6 and 7.—The first of these portions (18 cc.) was heterogeneous with a top layer (1 cc.) which was shown to be CS_2. Most of the lower layer was combined with the second portion (3 cc.), and fractionated yielding a central cut (3.5 cc.) believed to be pure CF_3SF_3, b.p. −7°, f.p. −110°, mol. wt., 160 (calcd., 158). The analysis, although roughly approximate, was unacceptable (S, 22.6%; calcd., 20.3%), but it should be stated that the technical difficulties involved in the microanalysis of compounds of this nature are very great.

Fraction 8.—This portion was partially crystallized at −80° and filtered by means of a filter stick yielding a residue (8 cc.) and a filtrate (12 cc.). The residue was redistilled, discarding a small forerun, and the remainder (about 8 cc.) had b.p. −10 to −9° at 168 mm., f.p. −52°, mol. wt., 242–263. This was refractionated and yielded a portion believed to be pure $SF_3CF_2SF_5$ (3 cc.), b.p. −20° at 90 mm., 26° (Siwoloboff), f.p. −51°, mol. wt., 265 (calcd., 266). The analysis, although closely approximate, was not entirely satisfactory (S, 23.4%, calcd., 24.1%). The filtrate on rectification yielded a portion (3 cc.), b.p. 17° at 550 mm., f.p. −72°, mol. wt., 236; and this on further fractionation gave a central cut of pure S_2F_{10} (1 cc.), b.p. −19° at 100 mm., 25° (Siwoloboff), (known[5] b.p. 29°, f.p. −92°). This very good sample liberated iodine from KI paper as expected, but froze twenty degrees higher than previously reported.

Anal. Calcd. for S_2F_{10}: S, 25.2; F, 74.8; mol. wt., 254. Found: S, 25.3; F, 75.1; mol. wt., 251.

Fraction 9.—This final portion was redistilled and yielded pure $SF_5CF_2SF_5$ (4 cc.), b.p. 23° at 170 mm., f.p. −70°. This portion was refractionated yielding a cut, b.p. 24° at 170 mm., mol. wt., 307, while the remainder was again redistilled in a small precision column yielding a central cut, b.p. 62° at 1 atm., from which the analytical sample was taken.

Anal. Calcd. for CS_2F_{12}: S, 21.1; mol. wt., 304. Found: S, 20.7; mol. wt., 307.

The analyses were by the Huffman Micro-analytical Laboratories, Wheatridge, Colorado.

DURHAM, N. C.

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Elevation of the Intrinsic Viscosity of Peanut Protein by Treatment with Terephthalyl Dichloride[2]

BY GODFREY E. MANN

RECEIVED FEBRUARY 16, 1953

It has been determined that the treatment of aqueous alkaline dispersions of peanut protein with the bifunctional acid chloride, terephthalyl dichloride (p-$C_6H_4(COCl)_2$), results in modified proteins of elevated intrinsic viscosity as measured at 25.0°, using 10 *M* urea as the solvent. The treatment also results in depression of the solubility of the protein in this solvent. The viscosity elevating effect appears to vary inversely with the temperature of the treatment; a greater rise occurring in the vicinity of 0° than at room temperature. At the low temperature the intrinsic viscosity of a protein preparation could be elevated to a maximum of about 6 times that of the original protein (from 0.24 to 1.5 deciliters/g.) while the solubility was maintained at 80% of the original. Under the same conditions, treatment with equivalent amounts of monofunctional benzoyl chloride did not lead to significant elevations of intrinsic viscosity.

Many organic and inorganic reagents have been used to harden or insolubilize proteins for industrial applications. In general, the mechanism of action for such reagents has been visualized as the formation of cross-links between neighboring protein molecules with the development of a tridimensionally stabilized structure, although denaturation of the protein might play an important role in some cases.[3,4]

Usually, the existence of cross-links in the treated protein has been inferred from analytical data and from the alteration in mechanical properties undergone by the protein upon treatment. Fraenkel-Conrat and Mecham,[4] however, demonstrated that treating a variety of proteins with formaldehyde resulted in elevations of the apparent molecular weights of the proteins as measured by osmotic pressure. Determination of sedimentation constants and light-scattering enabled Hughes[5] to demonstrate that a protein from human serum albumin forms a dimer when treated with mercuric chloride. There appear to be no viscosity data recorded on such protein derivatives of relatively unequivocal cross-linked structures.

The intrinsic viscosities of synthetic polymers have been related to such of their physico-chemical properties as molecular weights, molecular shapes and fiber-forming abilities.[6,7] Relationships between intrinsic viscosities and molecular weights and molecular shapes which have been established for proteins[8] make it appear that elevation of the intrinsic viscosity of a protein may markedly alter other of its properties, possibly resulting in enhanced fiber-forming capacity. This report describes the attainment of an increase in the intrinsic viscosity of peanut protein by treatment with the reagent terephthalyl dichloride (1,4-benzenedicarbonyl chloride), p-$C_6H_4(COCl)_2$. The bifunctional nature of the dichloride and the recognized reactivity of proteins toward aryl acyl chlorides[9] suggested that this reagent should be capable of

---

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at the National Meeting of the American Chemical Society, Atlantic City, N. J., September 14-19, 1952.

(3) J. Bjorksten, *Advances in Protein Chem.*, **6**, 343 (1951).

(4) H. Fraenkel-Conrat and D. K. Mecham, *J. Biol. Chem.*, **177**, 477 (1949).

(5) W. L. Hughes, Jr., *Cold Spring Harbor Symposia Quant. Biol.*, **14**, 79 (1950).

(6) B. L. Johnson and R. D. Wolfangel, *Ind. Eng. Chem.*, **41**, 1580 (1949).

(7) H. Mark, *ibid.*, **34**, 1343 (1942).

(8) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Pub. Corp., New York, N. Y., 1943, p. 512.

(9) R. M. Herriott, *Advances in Protein Chem.*, **3**, 169 (1947).