
 COMMUNICATIONS TO THE EDITOR

**THE QUANTUM YIELD OF CHLOROACETIC ACID
HYDROLYSIS**

Sir:

Following the report by Rudberg [*Z. Physik*, **24**, 247 (1924)] of a quantum yield of unity for the hydrolysis of monochloroacetic acid in aqueous solution at 2537 Å., this reaction has been employed in a number of cases as an actinometer.

A deviation in the results obtained with the uranyl oxalate and chloroacetic acid actinometers at 2537 Å. has led us to reinvestigate both reactions. A solution 0.01 *M* in uranyl sulfate and 0.05 *M* in oxalic acid gave an average quantum yield of 0.60, in agreement with the value reported by W. G. Leighton and Forbes for this wave length [THIS JOURNAL, **52**, 3139 (1930)]. For a solution 0.5 *M* in monochloroacetic acid, at 25° and an incident intensity of 2×10^{12} to 1×10^{13} quanta/mm.² sec., we find a quantum yield of 0.3 to 0.4 at 2537 Å. This result has been checked on two independent experimental set-ups, using different thermopiles and standard lamps as well as different samples of chloroacetic acid. Amount of hydrolysis was determined in both cases by potentiometric titration of the chloride ion. The results show some variability the source of which has not been located. There seems little doubt, however, but that under our conditions the quantum yield at 2537 Å. is much below unity, and we wish to call this to the attention of any who may be using or considering the use of this reaction as an actinometer.

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LOCATION OF OXYGEN IN CERTAIN STEROIDS

Sir:

In certain compounds of a steroid nature which occur in the adrenal gland there is an atom of oxygen which is exceedingly inert whether in the form of a ketone or of a hydroxyl group [Mason, Hoehn, McKenzie and Kendall, *J. Biol. Chem.*, **120**, 719 (1937)]. Consideration of the possible

locations for such an oxygen atom led to the conclusion that it must occupy position 11 or 12 of the steroid nucleus [Kendall, Mason, Hoehn and McKenzie, *Proc. Staff Meet. Mayo Clinic*, **12**, 136, 270 (1937); Steiger and Reichstein, *Helv. Chim. Acta*, **20**, 817 (1937)]. Steiger and Reichstein [*Helv. Chim. Acta*, **21**, 828 (1938)] have recently compared the acid (our acid 1) obtained by oxidation of corticosterone (our compound B) with the 3,11-diketo- Δ^4 -*etio*-cholenic acid prepared by degradation of digoxigenin and have found it to be different. They consider that this result casts doubt on position 11 as the location of the oxygen atom in question although it is not conclusive in view of the possible isomerism of the steroid skeleton. We have made a similar comparison with 3,12-diketo- Δ^4 -*etio*-cholenic acid and have found that the acid derived from corticosterone differs widely in its properties. This result eliminates the possibility that the oxygen atom in question occupies position 12 of a normal steroid nucleus. The close similarity of the behavior of this oxygen atom with that of the oxygen atom of sarmenogenin which has been assigned to C-11 argues for an identity of position. Degradation of sarmenogenin, which is known to differ from digoxigenin only in the configuration of 1 asymmetric center, probably C-9, should yield a definite answer to this problem.

The degradation of desoxycholic acid to 3,12-diketo-*etio*-cholenic acid has been described [Hoehn and Mason, THIS JOURNAL, **60**, 1493 (1938)]. Bromination in acetic acid solution gave 4-bromo-3,12-diketo-*etio*-cholenic acid, m. p. 197-198° (dec.); $[\alpha]^{25}_{D_{461}} + 109 \pm 2^\circ$. (Calcd. for $C_{20}H_{27}O_4Br$: C, 58.52; H, 6.64; Br, 19.42. Found: C, 58.40; H, 6.65; Br, 19.19.) This bromo acid lost hydrogen bromide when refluxed with pyridine to yield 3,12-diketo- Δ^4 -*etio*-cholenic acid, m. p. 205-207°; $[\alpha]^{25}_{D_{461}} + 240 \pm 5^\circ$. (Calcd. for $C_{20}H_{26}O_4$: C, 72.68, H, 7.93. Found: C, 72.35; H, 8.24.) Our acid 1 melts at 267-269°; $[\alpha]^{25}_{D_{461}} + 291^\circ$. Use of the methyl esters gave better yields and the final product was more readily purified. The ester of the bromo acid melts at 200-201°; $[\alpha]^{25}_{D_{461}} + 170 \pm 3^\circ$. (Calcd. for $C_{21}H_{29}O_4Br$: Br, 18.79. Found: Br, 18.94.)

Methyl 3,12-diketo- Δ^4 -*etio*-cholelate melts at 235–237°; $[\alpha]_{D}^{25} +242 \pm 2^\circ$. (Calcd. for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.25; H, 8.36.) The methyl ester of acid 1 melts at 178–179°; $[\alpha]_{D}^{25} +289 \pm 7^\circ$.

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NEW BOOKS

An Introduction to Microchemical Methods for Senior Students of Chemistry. By CECIL L. WILSON, M.Sc., Ph.D., Senior Assistant in Chemistry, The Queen's University of Belfast. Chemical Publishing Company of New York, Inc., 148 Lafayette Street, New York, N. Y., 1938. 196 pp. 93 figs. 12.5 × 19 cm. Price, \$3.00.

The book is written for the use of senior students in introductory courses on microchemistry. The author will acquaint the students "with the large field covered by microchemistry," but he has no intention of making the students capable "of undertaking advanced work utilizing microchemical methods." The scope of the proposed course is wide as may be derived from the following list of chapters: the compound microscope and its use (35 pp.), crystallization (6 pp.), observation of transition points and Liesegang rings (7 pp.), the polarizing microscope (16 pp.), classification of crystals (9 pp.), crystal tests (6 pp.), spot tests (8 pp.), inorganic qualitative analysis (29 pp.), inorganic gravimetric analysis (16 pp.), inorganic volumetric analysis (4 pp.), the tintometer (3 pp.), the colorimeter (6 pp.), the nephelometer (3 pp.), organic operations (12 pp.), residue- and Kjeldahl determinations (3 pp.), photomicrography (6 pp.), and the spectrograph (10 pp.). It is obvious that the number of suggested experiments must be small in every chapter.

The reviewer is of the opinion that the book would have gained in value if various rather unimportant discussions had been suppressed in favor of a more detailed description of the procedures. Nearly the whole page 169 is devoted to a discussion of the reasons for not including the more important determinations of quantitative organic elementary analysis, but a list of apparatus is missing, and the concentrations of the inorganic solutions listed in the appendix are not indicated.

The introduction contains the statement "...this was the acknowledged motive which first led Pregl to develop his invaluable work on organic microanalysis. Almost at the same time Emich was laying similar foundations in the inorganic branch, his work being at least in part inspired by the spectacular success attained by Pregl."

It may be permitted to recall the facts that Emich started his microchemical investigations before 1900, that Pregl did not enter the field before 1909 and acknowledged in his book that Emich had laid the groundwork, and finally that Pregl's "spectacular success"—obviously the Nobel Prize awarded in 1923—came far too late to have

any influence on Emich's numerous contributions to the development of microchemistry.

A. A. BENEDETTI-PICHLER

Katalyse und Determinismus. Ein Beitrag zur Philosophie der Chemie. (Catalysis and Determinism. A Treatise on the Philosophy of Chemistry.) By ALWIN MITTASCH. Verlag von Julius Springer, Linkstrasse 22–24, Berlin W 9, Germany, 1938. ix + 203 pp. 10 figs. 14.5 × 22 cm. Price, RM. 9.60.

This work consists of a discussion of general philosophical problems, especially those in the philosophy of science, *e. g.*, causality, determinism, organicism and teleology. The author takes account particularly of the bearing of what is now known about catalysis as a basis for his considerations. His standpoint is that of a physical chemist who has read widely and carefully in the literature of philosophy and who probably attaches more importance to philosophical speculation than do most chemists.

L. J. HENDERSON

Die Theorie der Komplexität und der Allotropie. (The Theory of Complexity and Allotropy.) By Dr. A. SMITS, Professor and Director of the Laboratory of General and Inorganic Chemistry of the University of Amsterdam. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1938. xii + 372 pp. 153 figs. 15.5 × 22 cm. Price, RM. 19.50.

The author states that he has set himself the task of setting forth the new material which has accumulated in the sixteen years since the appearance of his book on "The Theory of Allotropy," and of discussing it from the standpoint of the theory of complexity of phases. He has wished to include some of the topics treated in the earlier book, but for reasons of space has omitted some of the chapters, more particularly that chapter dealing in detail with the systems phosphorus and cyanogen.

The early chapters of the book set forth clearly the author's theory of phase complexity and his concept of pseudocomponents, with plentiful diagrams showing the relationship of the unary system at equilibrium to the pseudobinary or pseudoternary systems obtainable when the approach to internal equilibrium can be inhibited. Here, as also in later chapters, it is shown that recent theoretical work has postulated an increasing number of finer