reactions must all have highly polar transition states. Unsettled questions are whether any *rearrangement* or *racemization* reaction has any intermediate,[5] and, if so, whether it is the same as or different from the ion pair I involved in substitution. Special salt effects in these[4] and other[6] systems are consistent with but will be shown below not to require "intimate" ion pairs (II) as intermediates in rearrangement or racemization, preceding other "solvent-separated" ion pair intermediates (III) for substitution.

$$RX \rightleftharpoons \underset{II}{[R^+X^-]} \rightleftharpoons \underset{III}{R^+||X^-} \xrightarrow[\text{or } M^+Z^-]{HOY} \begin{matrix} ROY \\ \text{or } RZ \end{matrix}$$

To improve the chance of capturing an intermediate in one of these rearrangements (if any exists), we used the relatively unhindered and strongly nucleophilic salt lithium azide, rather than the perchlorates and arenesulfonates used previously. As a simple rearrangement we chose the oxygen equilibration reaction of trityl benzoate-*carbonyl*-O^{18} (RX) in dry acetone at 60°.

Without LiN_3 the equilibration reaction has a rate constant (k_1) of 3.8×10^{-6} sec.$^{-1}$. With 0.020 M RX and 0.006 M LiN_3, the initial rate of equilibration dropped to zero. After 8.7 hours, when LiN_3 was 41% consumed, there was 0% equilibration (experimental error ~ 2%) in recovered RX *vs.* 11% without azide. After 20 hours there was 11% equilibration *vs.* 24% without azide. The rate constant ($-\mathrm{d}\ \ln[RX]/\mathrm{d}t$) from following the disappearance of ionic azide was $4.4 \pm 0.4 \times 10^{-6}$ sec.$^{-1}$ both initially and after 10 hours, but $6.3 \pm 0.6 \times 10^{-6}$ with 0.010 M LiN_3. After 5 days, 95% of pure trityl azide was isolated from 0.013 M RX in a saturated (0.02 M) solution of LiN_3.

This competition experiment with LiN_3 proves rigorously that there is a capturable intermediate in this rearrangement distinct from RX, and that it is the same intermediate as for substitution by LiN_3. It is probably an ordinary ion pair I, $(C_6H_5)_3C^{+-}O_2CC_6H_5$. Within some or perhaps all such ion pairs, the oxygens interchange or become equivalent before further reaction occurs. We attribute the slight increase in rate (3.8 to 4.4) to a salt effect of LiN_3 on k_1. Earlier (more intimate) partly or totally equilibrated ion pairs are disproved because rearrangement was suppressed completely early in the reaction. Although prior ion pairs in which the oxygens are not equilibrated may occur, our results neither require nor suggest involvement of two types of ion pairs.

Previous results may also be interpreted in this simpler way without the dual ion-pair hypothesis (without both intimate ion pairs and solvent-separated ion pairs). The faster rate of racemization than of solvolysis of 2-*p*-anisyl-1-alkyl arenesulfonates (RX) in acetic acid even with much lithium perchlorate[6] can be due to reaction of $R^+ClO_4^-$ with LiX ion pairs to regenerate R^+X^-(I) and thence RX. The same kind of mechanism suffices for first-order exchange of benzhydryl chloride with radiochloride salts.[4] The superimposed second-order exchange can be a one-step reaction.

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(5) By intermediate we mean a species between reactants and products or one in equilibrium with a species between them but not a transition state or activated complex nor a reversibly formed by-product formed from one or more of the reactants or products by an entirely separate path.

(6) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954); S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958); S. Winstein, P. E. Klinedinst, Jr. and G. C. Robinson, *ibid.*, **83**, 885 (1961); S. Winstein, P. E. Klinedinst, Jr., and E. Clippinger, *ibid.*, **83**, 4986 (1961).

BOOK REVIEWS

Advances in Inorganic Chemistry and Radiochemistry. Volume 3. Editors, H. J. EMELÉUS and A. G. SHARPE, University Chemical Laboratory, Cambridge, England. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. ix + 463 pp. 16 × 23.5 cm. Price, $12.50.

The chapters in this volume are unrelated to each other and vary widely in length. They are reviews with numerous references and provide an excellent literature survey for those who are interested in the specialized subjects which were selected. It seems best to review each chapter separately. (1) "Mechanisms of Substitution Reactions of Metal Complexes" by F. Basolo and R. G. Pearson. The authors examine the results of numerous investigators, discuss the mechanisms for reactions and present many kinetic data in 33 tables (89 pp., 132 ref.). (2) "Molecular Complexes of Halogens" by L. J. Andrews and R. M. Keefer. After a historical introduction and a review of methods used for investigating complexes in solution, the authors discuss complex stabilities and the thermodynamics of the halogen complexes in a small number of organic solvents (40 pp., 158 ref.). (3) "Structures of Interhalogen Compounds and Polyhalides" by E. H. Wiebenga, E. E. Havinga and K. H. Boswijk. Thermodynamic data and structural parameters are presented for 12 interhalogen, and 28 polyhalides with univalent cations. The discussion is limited mainly to their crystal structure and molecular dimensions, and an explanation of the nature of the bonds (36 pp., 121 ref.). (4) "Kinetic Behavior of the Radiolysis Products of Water" by C. Ferradini. There is a brief introduction concerning the primary action of ionizing radiation, the mechanism of radiolysis of water and the rates of formation of radicals and products. He discusses in detail the rates of reaction of the OH radical and the H atoms with numerous ions and compounds (34 pp., 104 ref.). (5) "Silanes and Their Derivatives" by A. G. MacDiarmid. The methods of preparation, and physical and chemical properties of a large number of silane derivatives are presented in which the silicon is bonded to carbon, halogen, pseudohalogen, oxygen, sulfur, selenium, nitrogen, phosphorus and arsenic. Silyl–metallic compounds containing alkali metals, germanium, tin, boron or iron are also discussed briefly (49 pp., 208 ref.). (6)

"The General, Selective, and Specific Formation of Complexes by Metallic Cations" by G. Schwarzenbach. The author surveys the course of reactions when water molecules in the hydration shell of a metallic ion are replaced by other ligands "in order to point out some empirical regularities without giving more than an indication of their theoretical interpretation." In six tables are given formation constants for some well known complexes (28 pp., 70 ref.). (7) "Atmospheric Activities and Dating Procedures" by A. G. Maddock and E. H. Willis. This is an excellent review of the experimental techniques for the radiocarbon method of dating, critically examining the sources of error and the fundamental assumptions on which the method is based. The use of tritium for dating is also discussed (48 pp., 286 ref.). (8) "Polyfluoroalkyl Derivatives of Metalloids and Nonmetals" by R. E. Banks and R. N. Haszeldine. This chapter deals with the preparation, the chemical and physical properties of the known polyfluoroalkyl derivatives of mercury, boron, silicon, nitrogen, phosphorus, arsenic, antimony, oxygen, sulfur and selenium. Many of the data are presented in 20 tables (96 pp., 210 ref.)

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Microchemical Journal Symposium Series. Volume 1. Submicrogram Experimentation. Based on a Symposium Sponsored by the National Academy of Sciences and the National Research Council, Arlington, Virginia, May 15–18, 1960. Edited by NICHOLAS D. CHERONIS, Brooklyn College of the City University of New York. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1961. viii + 351 pp. 16 × 23.5 cm. Price, $12.75; $10.75 (paper).

This book contains the Proceedings of the Conference on Submicrogram Experimentation, a symposium limited to 29 participants. A total of 22 papers with discussions and a summary of the symposium are published here.

The submicrogram region is defined as that which includes masses from 10^{-6} g. to near the range of individual molecules. The methods used for study include activation analysis, emission spectrography, flame photometry, absorption spectrophotometry (ultraviolet, visible and infrared), mass spectrometry, X-ray spectroscopy and diffraction, fluorescence, density measurements, electrophoresis, magnetic susceptibility, micro- and macrobiological assay methods, enzymatic studies, paper chromatography, gas chromatography, olfactory sensing, microscopic examination (light and electron) and microcoulometry.

Diverse problems which necessitate working in this region include criminalistics, trace elements in high purity materials, marine chemistry, synthetic elements which are very limited in quantity, functions of trace substances in the growth of various organisms, carcinogenicity, serum analysis, atmospheric pollution, pesticide residues, analysis of tissue sections, and cytochemical studies.

As has been known for a long time, biological systems are very sensitive to small quantities of certain substances. Therefore, it is no surprise that much of the work in the submicrogram region has been done by investigators in the biological field. A large proportion of the papers in this book are biological in application. These studies most often involve trace quantities in large amounts of total sample, and separations are necessary before quantitative estimations are possible. Much of the effort in trace quantity studies is devoted to the separation of the desired material. Studies involving single cells and those on extremely limited quantities of sample deal with total quantities in the submicrogram region.

A few of the devices used are specially tailored for the small quantities, but many of the techniques consist of adaptations of existing equipment and instruments to handle the small quantities as may be seen from the list of the methods used.

Because of the diverse natures of the problems discussed, the book is extremely interesting. The fact that it is a compilation of individual papers given at a symposium yields a variety in styles of writing, in detailed content and completeness. The papers range from a rather thorough discussion of one phase of one technique (detector systems in gas chromatography) to more general descriptions of various techniques available. Very few of the papers contain sufficient detail to enable one to go directly into the laboratory and apply the technique. On the other hand, the book would be an excellent starting place for one interested in submicrogram analysis to find what techniques have already been devised.

In comparison to other books of this nature, the price may not be out of line, but none-the-less this reviewer feels that for the size and content this book is somewhat overpriced.

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Verfahrenstechnik in Einzeldarstellungen. Band 11. Experimentelle Vermessung von Dampf-Flüssigkeits-Phasengleichgewichten dargestellt am Beispiel des Siedeverhaltens von Fettsäuren. Von DR. R. MÜLLER, Hamburg, und DR. H. STAGE, Köln-Niehl. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany, 1961. viii + 117 pp. 15.5 × 23.5 cm. Price, DM. 21.—.

Measurements of the isobaric liquid–vapor equilibria give indications of the distillation behavior. This fact is of particular importance to the oil and fat industry. The authors have summarized in this book their work for a series of saturated even numbered, straight chain, fatty acids; these data supersede previous books describing experimental work in this field which are now out of date. The book consists of seven chapters and a total of 254 references through 1958. The authors have emphasized the newer types of apparatus which make such measurements not only much faster but also much less complex.

After an introduction and discussion of the importance of the determination of the vapor–liquid equilibria of fatty acids, the authors describe in Chapter II the operations involved in the preparation of pure fatty acids. They then discuss a number of previously used distillation columns; this leads into a detailed description of their distillation column with automatic control of distillation rate, heating temperature, distillation pressure, temperature of the cooling water, temperature registration, sample takeoff, etc. Descriptions are also given for the crystallization for the higher fatty acids from C_{14} on.

In Chapter III, the authors give the exact vapor pressure curves determined for the fatty acids from C_6 through C_{24} as well as tables of melting points. Chapter IV gives a detailed description of the authors' investigation of the temperature stability and sample analysis, in addition to phase equilibria for fatty acid mixtures of C_6–C_8, C_{10}–C_{12}, C_{14}–C_{16}, at various pressures; this is followed by tables of melting and solidification points for the same series of fatty acid mixtures. It also includes a discussion of the thermal stability of fatty acids at several temperatures with various lengths of heating time.

In Chapter V the apparatus used for the phase equilibria studies is described in detail. It is so constructed that the known source of error of previously described apparatus has been taken into consideration. This apparatus was tested by determining the equilibria for mixtures of acetone–benzene as well as 2-methylnaphthalene–decanone; the resulting values were checked by thermodynamic methods Equilibrium measurements of fatty acids included the mixtures: C_6–C_8, C_8–C_{10}, C_{10}–C_{12}, C_{12}–C_{14}, C_{14}–C_{16}. Each mixture was measured at three pressures. In order to evaluate these measurements, exact vapor pressure data were necessary. The literature values within the homologous series were checked and a formula was derived which gives vapor pressure curves for the higher fatty acids. The results of the vapor pressure measurements indicate that slight deviations from ideal behavior are found. This difference increases with falling temperatures. The association phenomena in these acids is discussed in this context.

The final two chapters include an evaluation of the reported results in terms of their thermodynamic significance as well as a discussion of further investigations which are necessary in this field.

Numerous tables for melting points, solidification points, vapor pressure curves and phase equilibria in addition to descriptions of the experimental apparatus used for these