From the dimensions found for the sodium oleate molecule, the volume is readily calculated—$V = 12.3 \times 7.56 \times 6.64$ cc. $\times 10^{-24}$. By multiplying by the specific weight (0.821), the weight of each individual molecule is obtained—507×10^{-24} grams. Hence a new method is found to calculate the number N of Avogadro, since the molecular weight is well known and equal to 304.35. In this manner we obtain for the number N the value, 6.003×10^{23}, while Millikan's last figure is 6.062×10^{23}. The probable error in our figure is 0.15 per cent., or

$$N = 6.003 \pm 0.08.$$

This method is probably the more direct, and is based only on Avogadro's definition of the number N. The details of this work, and a discussion of it, will appear shortly in the *Philosophical Magazine.*

P. LECOMTE DU NOUY

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH

THE AMERICAN CHEMICAL SOCIETY

DIVISION OF ORGANIC CHEMISTRY

R. R. Renshaw, *chairman*
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Introductory remarks: GILBERT N. LEWIS.

The mechanism of ester formation: JAMES F. NORRIS and FRANCIS B. STEWART. The velocity constants for the esterification of ethyl, normal butyl, secondary butyl and tertiary butyl alcohols with acetic and trichloroacetic acids with and without a catalyst were determined. The results show that the ratio between the constants in the uncatalyzed and catalyzed reactions for a given acid are about the same, whichever alcohol is used. On the other hand, in the case of any alcohol this ratio varies widely as the acid is changed. The results furnish experimental evidence for the conclusion that the catalyst functions through its action on the acid and not the alcohol. With the weak acid the influence of the catalyst is very great compared with its influence on the strong acid in increasing the rate of the reaction. The ratio of the velocity constants of the catalyzed reactions between a given acid and different alcohols is approximately the same as the ratio between the reactivities of the hydrogen atoms in the hydroxyl groups in these alcohols, and varies widely from the ratio between the reactivities of the hydroxyl groups. These facts show that in ester formation the hydroxyl group is furnished by the acid and the hydrogen atom by the alcohol.

Reactivity in acetal formation: HOMER ADKINS and E. W. ADAMS. The problem of the relationship between structure, reactivity (Michael) and rate of reaction has been studied by determining the equilibrium point and the rate with which it is reached, in the formation of about forty acetals. It has been established that there is no relationship between reactivity and rate of reaction. The reactivity and effect on rate of reaction of a number of groupings has been determined (eleven of the lower alkyls, phenyl in various positions, olefinic linkage, etc.). The significance of these facts in interpreting the mechanism of the reaction has been considered.

The mechanism of reduction in homogeneous solution: J. B. CONANT and H. B. CUTTER. The following types of reductions can be accomplished by such reducing agents as titanous chloride, vanadous chloride and chromous chloride; (1) reversible monomolecular reduction; (2) irreversible monomolecular reduction with or without cleavage; (3) reversible dimolecular reduction (formation of free radicals); (4) irreversible dimolecular reduction (pinacone formation). All these processes are conditioned by the reduction potential of the reducing agent, the hydrogen ion activity of the medium and the nature of the organic substance which in (1) and (3) can be measured as a potential. The irreversible processes probably proceed through a reversible phase which also has a characteristic reduction potential. Examples of (4) are the dimolecular reduction of benzaldehyde, and alpha, beta unsaturated ketones by vanadous salts.

Mechanism of vapor phase oxidation: R. T. HASLAM. This paper reviews the various theories offered for the mechanism of combustion of hydrocarbons. These theories are discussed in view of the existing experimental data on the subject and the theory that hydrocarbons burn by means of successive hydroxylations together with the importance of this concept is treated at some length. It is conclusively shown that the vapor phase oxidation of organic compounds other than straight chain hydrocarbons, although little studied, is different from the oxidation of the same compounds with liquid oxidizing agents. Some conclusions are drawn about the influence of substitution and of the relative position of groups in a molecule on their oxidability. As a practical application of the knowledge of the subject, it is shown how the burning of hydrocarbons can be improved by favoring the hydroxylation process, thus eliminating the formation of soot.

The mechanism of oxidation of organic compounds with potassium permanganate: WILLIAM LLOYD EVANS. This paper deals with mechanism of the oxidation of organic compounds in aqueous solutions by means of potassium permanganate alone, and also in the presence of added potassium hydroxide. The purposes of these oxidations have been to ascertain the several molecular stages through which certain organic compounds pass when they undergo this type of chemical change. These oxidations have been studied under chosen conditions of temperature and initial alkalinity with a view of ascertaining the effect of these variable factors on the course of the oxidation. The experimental results thus obtained have been used to deduce an appropriate mechanism which will best explain the observed oxidation phenomena. The following compounds have been made the object of such investigations: Ethyl alcohol, acetaldehyde, isopropyl alcohol, acetone, acetal, d-glucose, d-galactose, d-fructose, d-mannose, lactose, sucrose, maltose, cellose, mannitol, dulcitol and sorbitol. In all cases many of the theoretically possible intermediate compounds have been studied under exactly the same experimental conditions in order to aid in the determination of the exact course followed in these several reactions.

The mechanism of some Grignard reactions: HENRY GILMAN and co-workers. The reaction between R Mg X compounds and the so-called disulfoxides shows these compounds to have the thiosulfonic ester structure. With alpha disulfones and ketone-sulfones splitting occurs between the two characteristic groups. In connection with some studies on the electronic interpretation of reactions, preliminary experiments indicate that the Grignard reagent will not add to variously substituted ethylenic linkages.

The mechanism of the Friedel Crafts reaction: CECIL E. BOORD. The reaction products described by Mouneyrat, formed by the action of anhydrous aluminium chloride upon alkyl halides are used in the explanation of the Friedel Crafts reaction and extended to include the condensation of olefines with aromatic compounds in the presence of aluminium chloride.

(1) a $C_2H_5Cl + AlCl_3 = ClCH_2 - CH_2AlCl_2 + HCl$

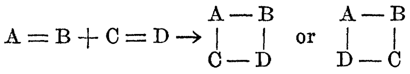
b $CH_2CH_2 + AlCl_3 = ClCH_2 - CH_2AlCl_2$

(2) $C_6H_6 + ClCH_2 - CH_2AlCl_2 = C_6H_5CH_2 - CH_2AlCl_2 + HCl$

(3) $C_6H_5CH_2 - CH_2AlCl_2 + H_2O = C_6H_5 - C_2H_5 + Al(OH)Cl_2$

A similar type of formulation is indicated for the condensation products formed by mercuric salts with olefines, since these react with aromatic derivatives to give condensation products which upon hydrolysis yield the alkylated aromatic derivatives. Zinc chloride also reacts with olefines to form addition products. These zinc chloride-olefine addition products condense with aromatic derivatives, particularly phenols, and by subsequent hydrolysis yield alkylated derivatives. These facts seem to indicate a similar mechanism for the condensation of monohydric alcohols with phenols in the presence of anhydrous zinc chloride.

The probable formation of 4-membered cyclic derivatives as intermediates in organic reactions: HAROLD HIBBERT and EARL M. BILGER. The views previously advanced by Hibbert and Montonna on the rôle of cyclic derivatives in ester formation (Tischtschenko reaction) and the synthesis of alpha chloro esters have been extended to the mechanism of reactions involving the synthesis of a wide variety of organic compounds. The theory assumes that when two derivatives containing unsaturated linkages react together the first stage of the reaction consists in the formation of a 4-membered ring.



$$A = B + C = D \rightarrow \begin{array}{c} A - B \\ | \quad\;\; | \\ C - D \end{array} \quad \text{or} \quad \begin{array}{c} A - B \\ | \quad\;\; | \\ D - C \end{array}$$

Such a ring system is characterized by the ease with which an atom (H; Cl) attached to atom A migrates to D (that is, from a 1- to a 5-position), this being accompanied by ring opening. The theory offers a simple explanation of the following reactions: (a) Acid chlorides and aldehydes; (b) aldol formation; (c) aldehydes with sodium nitro methane, hydrocyanic acid and sodium bisulfite; (d) guanidine and carbon bisulfide; (e) ethylene with organic and inorganic acid, phosgene, ureas and thioureas; (f) polymerization of styrene and methylene hydantoin; (g) ketenes and aldehydes.

GENERAL PROGRAM

Present status of the Crum-Brown-Gibson rule and a new theory of the mechanism of substitution in monosubstituted benzenes: E. M. TERRY and L. EICHELBERGER. Complete tables of the exact data on substitution in monosubstituted benzenes have been made. From these, briefer tables will be taken and shown. It will be seen that a new rule of substitution is justified. The fundamental basis of the new rule will be pointed out.

A chemical method for estimating the meta isomer in some disubstituted derivatives of benzene: A. J. HILL and A. W. FRANCIS. The method as applied to amino and phenolic compounds consists in titrating with a standard bromine solution. Meta compounds are tribrominated, while ortho and para compounds receive only two equivalents. The actual bromine consumption thus gives the percentage of the meta isomer. Nitro compounds are estimated by preliminary reduction with standard titanous chloride to the corresponding amino compounds, which are then titrated in the same solution with bromine. In some cases the solution must be cooled to zero to prevent oxidation or displacement of a group. The method has been applied successfully to twelve systems of isomers.

A comparative study of the Beckmann rearrangement of some hydroxamic acid derivatives: A. W. SCOTT. (1) The effect of temperature of the dry sodium, potassium and silver salts of the acetyl and benzoyl esters of hydroxamic acids derived from acetic acid, propionic acid and benzoic acid was studied. (2) The temperature of rearrangement in aqueous solutions of the sodium and potassium salts was also studied. The ease of the rearrangement seems to depend upon the influence of the hydrocarbon radicals of the acyl groups from which the hydroxamic acids were originally prepared. Including a similar study of isobutyl hydroxamic acid derivatives (Jones and Scott) (*J. A. C. S.*, 44, 407, 1921) the ease of the rearrangement in terms of the hydrocarbon radicals may be expressed in the following sequence: Phenol, isopropyl, ethyl, methyl.

Methyl ethyl sulfate as an alkylating agent: F. K. THAYER. (By title.) Methyl ethyl sulfate can be prepared only by reacting alcohol-free sodium methylate with an ether solution of the ethyl ester of chlorosulfonic acid. The yield is poor on account of side reactions. In order to obtain a comparison of the alkylating powers possessed by the methyl and the ethyl group, standard conditions were formulated by alkylating phenol with dimethyl sulfate. Under these standardized conditions phenol was alkylated with 1 mol. of ethyl methyl sulfate. Of the total amount of alkylation performed upon the phenol by $(CH_3)(C_2H_5)SO_4$, the methyl group was responsible for 80.2 per cent. and the ethyl group for 19.8 per cent.

Nitro-cresols and their mercury derivatives: G. W. Raiziss, A. Proskouriakoff and B. C. Fisher. One of the authors (Raiziss) has found previously in the study of mercuri-nitro phenols that the introduction of a nitro group into a certain organic compound of mercury greatly enhances the bactericidal properties of the latter. A similar biochemical study has been made by the authors on mercury derivatives of various mono-nitro-cresols. Ten nitro-cresols are theoretically possible, of which the authors prepared seven, also their organic mercury derivatives. While preparing these nitro-cresols, it was necessary in some instances to improve upon methods of preparation and purification of some of them. Better yields were secured, and purer products obtained. The mercuration of the nitro-cresols resulted in the preparation of new products. Some were obtained crystalline and very pure. This can not be always accomplished, as organic mercury derivatives of the type studied are difficult to isolate in pure crystalline form. Among the mercury derivatives one was found valuable from the biological viewpoint, the chemical name being 4-nitro-3, 5-bisacetoxymercuri-2-cresol. It is distinguished by its very high destructive action upon staphylococci, being employed now in the therapy of various infectious diseases with good results.

The reduction of oximes to amines: L. C. Raiford and E. P. Clark. The reduction of oximes with specially prepared sodium amalgam (Raiford and Clark, *J. A. C. S.*, 45, 1738 (1923)) in accordance with the directions previously reported (Science, N. S., 58, 471 (1923)) has been studied in nine additional cases. In each instance the compound has also been reduced with aluminium amalgam. In the latter case the water or dilute alcoholic solution of the oxime was usually allowed to stand over night with about two molecular proportions of the amalgam, after which the mixture was made alkaline with sodium hydroxide and distilled with steam. The amine was isolated as the hydrochloride. When sodium amalgam was used in acid solution, sodium acetate was used as a buffer, and the mixture kept constantly acid to litmus with acetic acid. When the liquid was kept alkaline to litmus, hydrochloric acid was used to neutralize the excess of alkali. With oximes containing aromatic radicals, the best results were usually obtained in the following order: Aluminium amalgam, sodium amalgam (alkaline), sodium amalgam (acid). With those containing aliphatic radicals, the order was: Aluminium amalgam, sodium amalgam (acid); while with sodium amalgam in alkaline solution, the action goes very slowly or not at all.

Organic mercury compounds obtained from naphthalic acid and other dibasic acids (Preliminary Paper): Frank C. Whitmore and G. J. Leuck. Heating the mercuric salt of naphthalic acid (naphthalene-1, 8-dicarboxylic acid) gives results similar to those obtained with mercuric phthalate, carbon dioxide being eliminated and a carbon-mercury linkage formed. The mercurated product reacts with acid to give very pure alpha naphthoic acid. Similar experiments have been carried out with nitronaphthalic acids. The 3-nitro compound reacts more rapidly than the unsubstituted substance and the 4-nitro compound reacts much more slowly. Treatment of the mercurated products with acid gives 6-nitro- and 4-nitronaphthoic acids, respectively. Similar studies are being carried out with diphenic acid and with a number of other dibasic acids, both aromatic and aliphatic, to find the effect of constitution on the reaction.

Action of organic mercury compounds with organic halides—II: F. C. Whitmore and N. Thurman. The action of mercury di-p-tolyl with 30 organic halides has been studied. In most cases there is no action even after refluxing the reactants in toluene for three or four hundred hours. Large quantities of materials were used so as to make possible and practically quantitative recovery of the unchanged substances. In some cases the mercury compound acted as a hydrocarbo base removing HX from the halide. Thus, ter-butyl bromide yields butylene. The only case in which halogen attached to carbon was found to act metathetically was diphenyl bromo-methane, which yields p-tolyl-diphenyl-methane. The analogous compound, diphenylene-bromo-methane, loses hydrobromic acid to give bis-diphenylene-ethylene. Of the various types of bases, such as hydro-bases like sodium hydride, ammono-bases like sodamide, aquo-bases like sodium hydroxide, and hydrocarbo-bases like the Grignard reagents and organic mercury compounds, the last named are by far the least active toward organic halides. However, when reaction does occur it is similar to that obtained with the other types of bases.

The preparation of halogenated benzoic acids from organic mercury compounds (Preliminary Paper; by title): F. C. Whitmore, G. Woodward and W. B. Gery. Mercurated benzoic acid is prepared either from benzoic acid or better from phthalic anhydride. Treatment with halogen gives the ortho halogen benzoic acid in good yield and high purity. Mercuration of product followed by treatment with same or different halogen gives di-ortho halogen benzoic acid. Para halogen benzoic acids are made from crude p-tolylmercuric chloride by permanganate oxidation to p-chloromercuri-benzoic acid, and subsequent treatment with halogen. Mercuration of the products followed by treatment with halogen gives ortho-para di-halogen acids. From these substances the tri-halogen benzoic acids will be prepared in similar way. The best method for making diphenic acid for another research has been found to be the treatment of methyl ortho-bromobenzoic acid prepared from phthalic anhydride as above, with metallic copper to give diphenic ester. The research is being continued with the carboxylic acids of naphthalene and similar substances.

J. A. Nieuwland,
Secretary

(To be continued)