Thus the motions of the planets do not prove the *truth* of the Einstein theory, nor, on the other hand, do they prove its *falsity*. While these motions can be accounted for by a certain distribution of matter in the solar envelope, it has not yet been established by observation that the matter is actually distributed through space in the required way. The presence of the matter is unquestioned; its distribution is still a problem of observational astronomy. In the present state of our knowledge regarding the distribution of this matter throughout space, the motions of the planets do not and can not furnish a definite answer to the question as to the validity of the Einstein hypotheses of relativity.

Charles Lane Poor

Columbia University,
April, 1921

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## THE AMERICAN CHEMICAL SOCIETY

(*Continued*)

### DIVISION OF ORGANIC CHEMISTRY

Rodger Adams, *chairman*
H. T. Clarke, *secretary*

*Arsenated benzophenone and its derivatives:* W. Lee Lewis and H. C. Cheetham. Benzarsonic acid is best prepared by reduction of p-nitrobenzoic and arsenation by means of Bart's reaction. With phosphorus trichloride and pentachloride, dichloro-p-arsinobenzoyl-chloride results. By means of the Friedel and Crafts reaction, benzophenone-p-arsenious oxide, arsenious acid, and arsonic acid are formed. The similar derivatives of 4-methyl benzophenone-p-arsenious oxide, 4-methoxy benzophenone-p-arsenious oxide, and 4-phenoxybenzophenone-p-arsenious oxide have been prepared. Their nitro compounds, oximes, and isomers are being studied. With arsanilic acid, dichloro-p-arsinobenzoylchloride gives the di-arsenated benzanilide. The further reactions of dichloro-p-arsinobenzoylchloride with hydrocarbons, ethers, phenols, and various amino- and hydroxy-compounds are being studied.

*6 chlorophenalphanapthazarsine and some of its derivatives:* W. Lee Lewis and C. S. Hamilton. 6 chlorophenalphanapthazarsine is prepared by heating phenyl alpha naphthylamine with arsenic trichloride. 6 cholorophenalphanapthazarsine with hydrogen peroxide gives phenalphanapthazarsinic acid. The sodium salt of this acid has been prepared. A series of compounds, 6 methoxyphenalphanapthazarsine, 6 ethoxyphenalphanapthazarsine, 6 propoxyphenalphanapthazarsine, 6 butoxyphenalphanapthazarsine, 6 phenoxyphenalphanapthazarsine are prepared by treating 6 chlorophenalphanapthazarsine dissolved in xylene with the corresponding sodium alcoholate. 6 bromophenalphanapthazarsine is prepared by refluxing 6 phenalphanapthazarsine oxide or 6 phenoxyphenalphanapthazarsine with hydrobromic acid. 6 phenalphanapthazarsine oxide is prepared from 6 chlorophenalphanapthazarsine by heating with silver oxide.

*Condensation reactions with benzyl cyanide:* Fred W. Upson and T. J. Thompson. Several phenyl alkyl succinic nitrils have been made by condensing benzyl cyanide either (1) with the cyanhydrine of the aliphatic aldehyde in the presence of sodium methylate, or (2) with the *a* brom ester of the fatty acid in the presence of sod-amide in ether suspension. Saponification of the resulting condensation products has given substituted succinic acids. The following have been made by method No. 2: methyl phenyl succinic acid, m.p. 185°; ethyl phenyl succinic acid, m.p. 194°; N. propyl phenyl succinic acid, m.p. 214°; and the following have been made by both methods: Iso-propyl phenyl succinic acid, m.p. 178°; iso-butyl phenyl succinic acid, m.p. 186°. The nitrils of the higher members can be saponified only under pressure. Some evidence has been obtained for the formula

$C_6H_5—\overset{H}{C}=C=N—Na$ for the sodium salt of benzyl cyanide.

*Derivatives of trihalogen tertiary-butyl alcohols. IV. The benzoic acid ester of tribromo-tertiary butyl alcohol or brometone benzoic acid ester:* T. B. Aldrich. The benzoyl ester of tribromo tertiary-butyl alcohol, $C_6H_5CO.OC—C_3H_6Br_3$, is prepared most conveniently by mixing molecular quantities of benzoyl chloride and preferably anhydrous tri-bromo tertiary butyl alcohol and heating on the steam bath until hydrogen bromide ceases to be given off. The ester is purified by heating on the steam bath with 5–10 per cent. caustic soda solution, washing with water, and finally recrystallizing from alcohol. It crystallizes in the monoclinic system and melts at 89–90°. It is readily soluble in the organic solvents, but insoluble in water. It is not so readily saponified as the aliphatic esters of either chloretone or bromotone. It is practically non-volatile at either incubator or room temperature, and is not volatile with steam to any extent. In general its properties are the same as the corresponding ester of trichlorotertiary butyl alcohol. Analytical data show its composition to be $C_{11}H_{11}O_2Br_3$.

*Trihalogen-methyl reactions. IV. Tetrachlorosuccinic acid:* **HOWARD WATERS DOUGHTY** and **BENJAMIN FREEMAN**. Tetrachlorosuccinic acid is formed by the action of trichloroacetic acid on copper dust in benzene solution. It is a hygroscopic solid which is not very stable, being easily hydrolyzed. The aniline salt (m. p. 149°) and ethyl ester (b. p. 156°/13 mm.) are described. Ammonium trichloroacetate reacts vigorously with copper in aqueous ammonia, losing two atoms of chlorine per molecule. This action also takes place still more vigorously with cadmium and zinc, but not with silver.

*Spiro-pyrimidines. II. Cyclohexane-1, 5-spiro-pyrimidines:* **ARTHUR W. DOX** and **LESTER YODER**. Cyclohexane-1, 1-dicarboxylic ester, prepared by condensation of 1, 5-dibromopentane with ethyl malonate, condenses with urea and with guanidine to form cyclohexane-1, 5-spiro-pyrimidines. These products are very similar in their properties to the corresponding cyclobutane-1, 5-spiro-pyrimidines previously described by the writers. In certain respects they resemble also the dialkylbarbituric acids, but differ from the latter in having a carbon atom common to two rings.

*Spiro-pyrimidines. III. Cyclopropane-1, 5-spiro-pyrimidines:* **ARTHUR W. DOX** and **LESTER YODER**. Cyclopropane-1, 1-dicarboxylic ester, prepared by condensation of ethylene bromide and ethyl malonate, might be expected to condense with urea and substituted ureas and yield spiro-pyrimidines analogous to those obtained from cyclobutane- and cyclohexane-1, 1-dicarboxylic esters. Condensations with urea and with guanidine were readily effected, but the products were invariably amorphous, insoluble substances of great stability. Analyses showed the same percentages of nitrogen as those calculated for the simple spiro-derivatives. It is probable that the cyclopropane ring opens and two or three molecules unite to form a cyclobutane or cyclohexane nucleus with two or three barbituric acid groups attached. The polymer obtained from urea could not be hydrolyzed by long boiling with concentrated hydrochloric acid. Hydrolysis by means of sodium hydroxide gave an acid which lost carbon dioxide on heating, with formation of a crystalline acid, of melting point 151° and neutralization equivalent 86.

*Pyrimidines from dialkylmalonic esters and benzamidine:* **ARTHUR W. DOX** and **LESTER YODER**. In the presence of sodium ethylate at 70–75°, dialkylmalonic esters condense with benzamidine to form derivatives of tetrahydropyrimidine. The dialkyl-malonic esters used were the dimethyl, diethyl, dibutyl, diisoamyl, and dibenzyl. These all gave white products. The corresponding monoalkyl derivatives were bright yellow. The latter may therefore be regarded as possessing the tautomeric enol structure.

*An electrochemical study of certain reversible reductions:* **J. B. CONANT** and **H. M. KAHN**.

*The reactivity of the chlorine atom in the nitrobenzyl chlorides:* **J. B. CONANT** and **S. S. NEGUS**.

*The 1.4-addition of phosphenyl chloride:* **J. B. CONANT** and **S. M. POLLACK**.

*A comparative study of ring stability:* **NAO UYEI** and **OLIVER KAMM**.

*Investigation of isomerism in the diphenyl series:* **J. H. WALDO**, **C. S. PALMER** and **O. KAMM**. Fixation of the benzene nuclei in diphenyl derivatives according to the Kaufler-Cain theory leads to the possibility of optical isomerism in the case of certain diphenyl derivatives. Salts of diphenyl-O-carboxylic acid with optically active bases were subjected to crystallization but there was found no conclusive evidence of this type of isomerism. The investigation has been extended also to benzidine derivatives, particularly to benzidine disulfonic acid. The negative results obtained fail to support the recently proposed theories concerning the structure of the diphenyl derivatives.

*The action of hydrogen sulphide upon tri-nitro-toluene:* **F. J. MOORE** and **E. H. HUNTRESS**. In this reaction Cohen and Dakin observed the formation 2-6-di-nitro 4- tolyl hydroxylamine which when boiled with hydrochloric acid yielded a colorless solid which they assumed to be the amine, but later denied this without further characterizing it. They subsequently obtained the true amine by the addition of hydriodic acid. The observation that the above hydroxylamine yields this same compound when treated with silver nitrate raised the suspicion that it might be the azoxy compound. This accounts for the oxygen which ought to have been evolved in the original equation of Cohen and Dakin, for we have shown that 2-6 dinitro-4-tolyamine is formed at the same time.

*The constitution of the secondary product in the sulphonation of cinnamic acid:* **F. J. MOORE** and **RUTH M. THOMAS**. The principal product of the reaction is para-sulpho-cinnamic acid. With this is formed an isomer whose barium salt is much more soluble. This has hitherto been variously described as an ortho and a meta compound. It has been supposed to be different from the meta compound prepared by Kaffka from m-sulpho benzaldehyde by the Perkin synthesis. We have shown that it is identical, and also that on oxidation with permanganate it yields meta sulpho benzoic acid. It can be easily characterized by the melting points of its aniline and toluidine salts.

*Separation of aromatic primary and secondary amines:* I. N. Hultman and H. T. Clarke. The separation of primary and secondary amines can in most cases be carried out satisfactorily by taking advantage of the solubility in alkali of the benzenesulfonyl or toluenesulfonyl derivatives of the primary amines. The recovery of the base from such derivatives is however apt to be troublesome, and in certain instances difficulties are met with in the alkali treatment owing to the ease with which the sodium salts are hydrolyzed. Thus they can be extracted from their solution in alkali merely by shaking with ether; and in cases where only a small quantity of primary base is present, the sulfonyl derivative of the secondary amine acts in the same way as an extracting solvent. This was found to be the case particularly with p-toluidine and its monomethyl derivative. This mixture moreover can not be separated by treatment with zinc chloride solution, as is possible in the case of aniline and methylaniline, since methyl-p-toluidine appears to form an insoluble zincichloride. Advantage can therefore be taken of the observation that primary aromatic amines, on heating to 160–180° with urea are converted into symmetrical diarylureas, while secondary bases, typified by methylaniline, do not react at all with urea. It is thus merely necessary to heat the mixed bases with urea in slight excess over the calculated amount, and treat the product with dilute acid.

*Potassium derivatives of the alkyl amines:* Edward C. Franklin. By the action of metallic potassium on methyl amine, ethyl amine and dimethyl amine in the presence of platinum black, the compounds represented by the formulas $CH_3NHK$, $C_2H_5NK$ and $(CH_3)_2NK$ have been prepared.

*The existence and reactions of positive halogens attached to carbon in aromatic compounds:* Ben H. Nicolet. W. A. Noyes, J. Stieglitz, L. W. Jones and others have interpreted and contributed a large amount of data on the positive nature of halogen attached to nitrogen. Howell and Noyes have shown the I of $C_2I_2$ to be positive. It is now shown that a number of compounds, most typically p-iodoaniline and 3-iodo 4-toluidine, can be hydrolyzed with acids in such a way that the halogen is replaced by hydrogen, and that the halogen resubstitutes to give di-halogenated products—two proofs of positivity. Such halogens appear to be readily removed (replaced by hydrogen) by heating with $SnCl_2$ and HCl.

*Diphenyl-β-naphthylemethyl:* M. Gomberg and F. W. Sullivan, Jr. Diphenyl-β-naphthylmethyl was prepared and found to exhibit the characteristic chemical reactions and physical properties of free radicals. Determinations by the cryoscopic method showed that dissociation increased with rising temperature and with dilution. Contrary to the theory that the color of free radical solutions is due to dissociation of the dimolecular to the monomolecular form, investigation by colorimetric methods showed that the increase in color intensity was quite independent of changes in dissociation. It was also found that not more than one third of the monomolecular free radical was in the colored form. From these facts we believe that the color of solutions of free radicals is best explained on the assumption that the dimolecular form dissociates to the mono-molecular form in which equilibrium exists betweeen the colorless benzenoid and the colored quinonoid tautometer.

*Contribution to the structure of benzidine: Formation of rings through the m and p positions of benzene:* Roger Adams and W. C. Wilson. Benzidine condenses readily with aromatic dialdehydes or ketones of the type represented by terephthalaldehyde and resodiacetophenone, to give condensation products which analyze for one molecule of benzidine plus one molecule of dialdehyde with the elimination of two molecules of water. It is barely possible that these substances consist of two molecules of benzidine with two molecules of dialdehyde, with the elimination of four molecules of water. The substances are too insoluble to allow the molecular weight to be obtained. If these substances are of the simpler type, it is difficult to see how Kaufler's formula for benzidine can be accepted, since his structure assumes that the amine groups are as close together as the amine groups in ophenylenediamine. Benzidine also condenses with the monazine of terephthalaldehyde to produce a product which analyzes for one molecule of each with the elimination of two molecules of water. It is apparent that ring structures containing a very large number of atoms and connecting the meta and para positions in the benzene nucleus are readily prepared.

*The preparation of dihydrobenzene and some of its derivatives:* E. C. KENDALL and A. E. OSTERBERG. The use of certain sulfonic acids for the dihydration of quinite or of tetrahydrophenol. The yield of dihydrobenzene from quinite by catalytic action of phenolsulfonic acid is practically quantitative. Dihydrobenzene Δ 1: 4 adds hydrochlorous acid and halogens.

*Stability of the C-Hg linkage in mercury derivatives of anisole and phenetole:* EDMUND B. MIDDLETON and F. C. WHITMORE. The stability of this linkage resembles that of the corresponding linkage in acetylated mercury derivatives of phenol. While the C-Hg linkage in mercury compounds containing a phenolic hydroxyl is broken quantitatively by inorganic iodides and similar reagents the C-Hg linkage in the anisole and phenetole compounds is stable to these reagents. The ortho anisyl and phenetyl mercuric halides give the corresponding $R_2Hg$ compounds. The para compounds form the iodides which remain unchanged. Potassium sulfocyanate gives the same results as the iodides with mercurated phenols, their acetyl derivatives, and mercurated anisoles and phenetoles.

*Preparation of mercury ditolyl from tolymercuric chloride:* L. FRANCES HOWE and F. C. WHITMORE. Tolylmercuric chloride prepared from toluene sulfinic acid obtained from p-toluene sulfone chloride was treated with the reagents usually used for changing compounds of the type RHgX to those of the type $R_2Hg$. Metallic copper in alcohol and sodium stannite in water gave very poor yields. Sodium in xylene, aqueous sodium sulfide, and aqueous sodium thiosulfate gave fair yields. Potassium iodide gave an almost quantitative yield. A new reagent for this purpose, potassium sulfocyanate, gave almost as good a yield. Using the sulfone chloride obtained from saccharine manufacture this method is the most convenient for making a mercury diaryl.

*Organic compounds prepared from ortho-chloromercuribenzoyl chloride:* F. C. WHITMORE and EDMUND B. MIDDLETON. *Preliminary paper.* The acid chloride obtained by the action of thionyl chloride on the anhydride of ortho-hydroxymercuribenzoic acid reacts with alcohols and amino compounds giving mercurated benzoic esters and amides. Compounds have been prepared from methyl alcohol, ammonia, aniline, and p-aminobenzoic acid. These compounds are too insoluble for therapeutic use. The action of more complex alcohols and amino compounds is being studied.

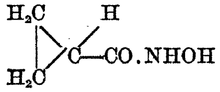
*Mercury compounds of normal-butyl:* RUTH WALKER and F. C. WHITMORE. n-butyl bromide reacts with dilute sodium amalgam giving a poor yield of mercury dibutyl. Mercuric chloride reacts with butyl magnesium bromide in excess, forming butyl mercuric bromide, calomel, and a small amount of mercury dibutyl. Using an excess of mercuric chloride gives a good yield of butyl mercuric bromide. Heating this substance with an excess of butyl magnesium bromide gives a fair yield of mercury dibutyl, a liquid boiling at 215°. The halide reacts with silver oxide and water giving a water solution of butyl mercuric hydroxide, a strong base. Treatment of this water solution with solutions of sodium halides gives precipitates of the butyl mercuric halides. The mercury butyl compounds are extremely toxic.

*Mercury derivatives of meta-nitrobenzoic acid. Preliminary paper:* F. C. WHITMORE and V. E. MEHARG. Nitrobenzoic acid fused with mercuric acetate gives a mixture of organic mercury compounds which are stable to sulfides. One of the compounds is 4-Hydroxymercuri-3-nitrobenzoic acid. The position of the mercury is proved by conversion into 4-bromo-3-nitrobenzoic acid. The mercury compounds are soluble in sodium hydroxide and in sodium carbonate. The solution in alkali causes a partial breaking of the C-Hg linkage. The mercury compounds and their reactions are being studied further.

*The quantitative determination of paraformaldehyde:* PARRY BORGSTROM and W. GRENVILLE HORSCH. Paraformaldehyde was analyzed by four methods and gave by (1) "neutral sulfite" 96.7 per cent., (2) iodimetric 96.7 per cent., (3) oxidation by dichromate, titration of excess 96.3 per cent., (4) oxidation by permanganate (or dichromate) with absorpton of $CO_2$ 96.9 per cent. formaldehyde. For the "neutral sulfite" use 0.5 $N$ to 1.0 $N$ sulfuric or hydrochloric acid, rosolic acid as indicator and 4 $N$ freshly prepared sodium sulfite. In the "iodimetric" method, the base is first added to the paraformaldehyde, then the iodine solution (0.2 $N$) within one minute time interval. Increasing this time or changing the order in which the reagents are added lowers the apparent formaldehyde content considerably. The remainder of the analysis is as usual. With other methods, ordinary precautions should be observed.

*Rearrangements of some new hydroxamic acids related to heterocyclic acids and to diphenyl and triphenylacetic acid:* Lauder W. Jones and Charles D. Hurd. Hydroxamic acids of thiophene and furane alpha carboxylic acids yield silver salts of their acyl derivatives which are less readily rearranged than the corresponding derivatives of benzhydroxamic acid. Diphenyl- and triphenylacethydroxamic acids were also examined, and it was found that an increase in the number of phenyl groups occasions greater readiness to rearrange. Diphenylacethydroxamic acid is formed by the action of diphenylketene upon hydroxylamine—a new type of reaction. Triphenylacethydroxamic acid is not produced by the interaction of ethyl triphenylacetate with hydroxylamine, but is quantitatively formed from the acid chloride.

*The hydroxamic acid of cyclopropane carboxylic acid and its derivatives:* Lauder W. Jones and Alfred W. Scott. The monohydroxamic acid



was prepared in order to determine what effect the trimethylene ring would have upon the Beckmann rearrangement of this compound and some of its derivatives. The hydroxamic acid is a colorless solid which melts at 123°. The benzoyl ester (*A*) $C_3H_5$—CO.NHO.CO.$C_6H_5$ (m. p. 149°) and the acetyl ester (*B*) $C_3H_5$—CO.NHO.CO.$CH_3$ (m. p. 106°), as well as the potassium, sodium and silver salts of these esters were studied. When the salts of (*A*) were heated gently, they decomposed to give cyclopropane isocyanate and the corresponding benzoates. Their relative stabilities increased in the order given above. When the salts of the alkali metals were heated with water, they showed a pronounced tendency to hydrolyze, which made it difficult to control the reaction so that the usual product of rearrangement, a sym-disubstituted urea, could be obtained. Unexpected stability was encountered in the case of the potassium salt of the acetyl ester (*B*) which is but little decomposed at 190°. The silver salt of this ester, unlike silver salts, was readily soluble in a mixture of alcohol and water, or in water alone.

*The preparation of phenyl acetylene:* John C. Hessler. Nef's method of preparing phenyl acetylene was to heat ω-bromstyrene in a sealed tube with alcoholic potassimu hydroxide. He used only a small quantity of alcohol in order to minimize the yield of the by-product, phenyl-vinyl ethyl ether. The writer's method is to allow the bromstyrene to flow, drop by drop, upon molten caustic potash contained in a flask heated in an oil bath at 200 to 220°. The phenyl acetylene distills over as it is formed, carrying with it only traces of unchanged bromstyrene. Yield: 80 per cent. of the theory of purified product.

*On a quantitative study of the Grignard reagent:* H. Gilman, P. D. Wilkinson and W. P. Fishel. In connection with some work on the addition of the Grignard reagent to ethylenic hydrocarbons, a method for the quantitative estimation of this reagent was found desirable. For this purpose a number of methods are being investigated, among them, (1) titration with iodine, (2) an indirect analysis involving the determination of the magnesium and alkyl halide actually used, and (3) an extension of the Zerewitinoff method involving the measurement of hydrocarbons given off when the Grignard reagent is treated with a compound containing "active" hydrogen. The first of these methods, that of titration with iodine, has been found unsuitable. In this connection the optimum conditions for the formation of the Grignard reagent are being studied.

*A simple type of glass pressure bottle:* R. R. Read. The apparatus consists of a simple adaptation of the common soda siphon to the purpose of a glass pressure flask.

*An indirect method of mercurization of organic compounds and a method of carbon linking:* Morris S. Kharasch. The method consists of heating the mercury salts of carboxylic acids, which lose carbon dioxide readily, the mercury then taking the position originally occupied by the carboxyl groups. Also, since the mercury can be readily replaced by a halogen, the method enables one to substitute a carboxyl group by a halogen. It was also found that the mercury compounds thus formed, especially those of the aliphatic series, can be made to split off mercury, thus linking the two carbon atoms. In the aromatic series, in the case of carboxylic acids which do not lose carbon dioxide readily, the mercury usually orients ortho to the carboxyl group. However, if a negative group is present in the molecule, the mercury orients itself ortho to that group, irrespective of the position of the negative group. In this respect, a number of substituted benzoic acids have been investigated.

Charles L. Parsons,
*Secretary*