At present there seems to be no adequate theoretical method for calculating the free energy of ionization of an organic acid,[11] hence methods which have been suggested for calculating or representing the effect of substituents upon the ionization constant of such an acid are approximate. While Smallwood[12] met with some success by attributing the change to the electric moment associated with the substituent, he obtained particularly bad results with the acids studied in this paper. MacInnes[13] has shown that log K for certain substituted acids, including the ones here studied, is nearly a linear function of d^{-1}, where d is taken as the distance between the polar bond joining the carboxyl group to the chain or ring and the polar bond connecting the substituent to the chain or ring. If the d's be taken as the ratios of the distances across a regular plane hexagon for the *ortho*, *meta* and *para* acids, namely, $1:\sqrt{3}:2$, these three acids give a straight line when log K is plotted against d^{-1} and the equation for the line is

$$\log K = -5.0471 + (2.1249/d) \qquad (16)$$

This equation reproduces the values of K to within ±0.31%, but, as MacInnes has observed, the constant is not log K for the unsubstituted acid. This behavior of the substituted acids might be considered to point to a plane, regular, hexagonal structure for these substances, but, even if the relation used could be developed in a forthright way, the values of log K for the *meta* and *para* acids are so nearly equal that this indication should be given little weight. Our own attempts to develop an exact theory of the ionization of the weak electrolyte have been unsuccessful.

Summary

The conductances of aqueous solutions of benzoic acid, *o*-chlorobenzoic acid, *m*-chlorobenzoic acid, *p*-chlorobenzoic acid and the sodium salts of the first three acids have been measured at 25°.

From these results and our previous measurements on hydrochloric acid and its sodium salt the following ionization constants have been found

C_6H_5COOH $K = 6.295 \times 10^{-5}$
o-ClC_6H_4COOH $K = 1.197 \times 10^{-3}$
m-ClC_6H_4COOH $K = 1.506 \times 10^{-4}$
p-ClC_6H_4COOH $K = 1.04 \times 10^{-4}$

The results with the strong electrolytes again confirm Onsager's equation as a limiting law and Shedlovsky's extension of the equation to the moderately dilute solutions. The results with the weak acids again show that the theoretical constant of the limiting law of Debye and Hückel correctly represents the dependence of the activity coefficient of these acids upon their ionic concentrations.

At present, there is no adequate theoretical method of calculating the ionization of a weak electrolyte from its structure.

NEW HAVEN, CONNECTICUT RECEIVED JULY 10, 1934

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[11] For a discussion of the several factors involved see Briegleb, *Z. physik. Chem.*, **10B**, 205 (1930).

[12] Smallwood, THIS JOURNAL, **54**, 3048 (1932).

[13] MacInnes, *ibid.*, **50**, 2587 (1928).

NOTES

Notes on the Movement of a Borax Bead on Platinum Wire

BY J. L. CULBERTSON

Anyone who has had occasion to use the borax bead on a platinum wire in the qualitative laboratory is familiar with the method by which the bead may be driven from one part of the wire to another by means of the flame. This is accomplished by heating one side of the bead on holding it in the edge of the flame. So heated the bead will recede from the hotter side and by drawing the wire through the flame as rapidly as the bead recedes the movement may be continued to the end of the wire. This phenomenon is exceedingly common and yet the writer has been unable to find in the literature any analysis of the situation based on a consideration of the surface tensions acting in the system. That such an analysis may be appropriate is suggested by the observation that the contact angle of the liquid bead on the surface of the platinum is much greater when at high temperatures than when at lower ones. No measurements of these contact angles have been made but the fact that the angle changes, as indicated, with temperature change is readily verified by even the most casual observation. This may be most readily accomplished by studying the form of a small globule of borax on a piece of platinum foil. When enveloped in a Bunsen flame the globule will draw up into a form almost hemispherical but on withdrawing it from the region of high temperature the borax is observed to spread into a comparatively thin layer. The spreading is probably arrested by the increased viscosity and rigidity of the cooling mass. The bead on the wire may, somewhat less readily, be observed to undergo the same changes.

Let us consider an application of the equation of Thomas Young to the point of contact of the bead with the platinum wire. This equation reads as follows: $S_1 = S_{12} + S_2 \cos \Theta$, where S_1 is the surface tension of the solid, S_{12} is the interfacial surface tension (solid–liquid), S_2 is the surface tension of the liquid and Θ is the angle of contact of the liquid with the solid. Of course the equation cannot be applied quantitatively but the significance of a change in Θ can be estimated. Rewriting the equation as $S_1 - S_{12} = S_2 \cos \Theta$ it seems apparent that an increasing value of Θ indicates that the $S_1 - S_{12}$ difference is decreasing more rapidly that the surface tension of the liquid, or in other words the adhesion tension[1] of the borax–platinum system is decreasing with increase of temperature.

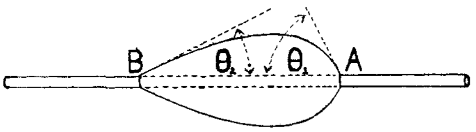

Fig. 1.

Now referring to the figure and assuming that heat is applied at A it is obvious that an increase in the contact angle Θ_1 on the hot side of the bead will tend to shorten the longitudinal dimension of the latter, causing it to swell and thereby increase the angle Θ_2 on the cool side of the bead. Furthermore, it is to be expected that the surface tension of the liquid will be lower on the hot side of the bead than on the cool side and on this account the surface layer of the drop will be drawn toward B. This will also tend to increase the angle Θ_2 except in so far as the surface movement is offset by the counter-circulation within the bead. The increase in Θ_2 at B will alter conditions at that point and if a dynamic equilibrium actually existed there, readjustment will be made by the movement of the line of contact toward the left, which will tend again to lower the magnitude of the angle Θ_2. If therefore a temperature differential is maintained between A and B, this readjustment process will be made continuous and the bead will creep along the wire from hot to cool regions. This latter is exactly what we find does occur and our analysis seems to indicate that in such a system the formation of contact angles is the result of a dynamic equilibrium of surface forces.

THE LABORATORY OF PHYSICAL CHEMISTRY
STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON
RECEIVED MARCH 16, 1934

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[1] Freundlich, "Colloid and Capillary Chemistry," p. 157.

The Preparation of Phenyl Mercuric Nitrate

BY G. H. WOOLLETT AND V. A. COULTER

Diphenyl mercury in chloroform when shaken vigorously with aqueous mercuric nitrate solution is converted into phenyl mercuric nitrate. The entire mixture may later be dissolved in boiling alcohol for crystallization, giving a 75% yield of nearly pure material, m. p. 188° dec. The residue left after melting decomposes explosively at about 270°. The following quantities have proved to be in best proportion: $HgNO_3 \cdot 0.5H_2O$ 3.49 g., chloroform 50 cc., diphenyl mercury 3.54 g. (0.01 mole), water 3 cc. and alcohol 600 cc. The solubility of phenyl mercuric nitrate at 5° and at the boiling point of the solvent (g. per 100 cc.) is as follows: water 0.05; 0.90; alcohol 0.08; 0.51.

UNIVERSITY, MISS.
RECEIVED APRIL 16, 1934

An Unknown Radioactivity

BY A. V. GROSSE

Three years ago, during our unsuccessful search of an isotope of element 91 of long life,[1] we noticed in two zirconium minerals (eucolite and eudyalite from Greenland) a small α-activity, which behaved chemically identically or very like protactinium, the origin of which was difficult to account for.

In the meantime the relationship between protactinium and uranium has been definitely established and the fact confirmed that in every uranium mineral, disregarding age, origin or uranium concentration, 1 g. of uranium contains in equilibrium $2.7_8 \cdot 10^{-7}$ g. of Pa, equalling $27._9$ mg. of U_3O_8 in α-activity.[2,3]

In the minerals mentioned the amount of α-

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[1] A. V. Grosse, *Naturwissenschaften*, **20**, 505 (1932).

[2] A. V. Grosse, *Phys. Rev.*, **42**, 565 (1932).

[3] A. V. Grosse, *J. Phys. Chem.*, **38**, 487 (1934).

activity, with the chemical properties of element 91, was present in about 10 × greater quantity than the natural protactinium content of the mineral, as deduced from the uranium content.

Recently this phenomenon could be checked with much greater ease than in our first electroscopic measurements, by means of a pliotron-tube α-particle counter, thanks to the assistance of Mr. H. Doolittle of the Physics Department.

Since contamination by protactinium is naturally the greatest source of error, blanks were run simultaneously with the analyses using the same chemicals (in equal amounts) and the same utensils.

The results obtained with the eudyalite, of which we had large amounts, are given below:

1. Chemical composition: corresponds to a sodium calcium zirconosilicate; contains besides SiO_2, Na_2O, CaO and ZrO_2 (5.37%), also FeO, MnO, K_2O, HfO_2 and in smaller quantities H_2O, Cl, Y, La and other rare earths, Ti, Nb, Ta, Ni, As, Mo, Sr, Zn, Pb, Th and U.

2. Uranium and radium content: 1.00 g. of eudyalite contains: $<5.4 \cdot 10^{-5}$ g. of uranium (x-ray determination, W. Noddack - A. V. Groose); 1.00 g. of eudyalite contains: $1.26 \cdot 10^{-11}$ g. of radium, corresponding to $3.8 \cdot 10^{-5}$ g. of uranium (Ra-Em method, R. Evans; same value was also found by Lord Rayleigh[4]).

3. Theoretical Pa content $(=N)$: 1.00 g. of eudyalite should contain in equilibrium Pa $=$ $1.06 \cdot 10^{-3}$ mg. of U_3O_8 in activity, or (since 1 mg. U_3O_8 emits in all directions 20.1 α/sec.) 62 α-particles from Pa/hour $= N$.

4. Unknown activity: the data on our three determinations, together with the blanks, are correlated in the table below. The amount of unknown radioactivity per gram of eudyalite is given in column 5; it is less than 3% of the total activity of the mineral.

It is difficult to explain the origin of this activity. The possibility of contamination during our analyses seems to be excluded as the blanks indicate, although in this difficult field further determinations would be desirable. The leaching of uranium or infiltration of protactinium from outside the mineral is very improbable in the light of all our geochemical knowledge, in the view of the normal radium content, as well as the fact of the chemical properties of protactinium and the primary nature of the mineral.

Because of the fact that the activity must have a recent source of formation, we tentatively suggest that it might be due, either directly or indirectly, to cosmic rays. Little is known about the laws of interaction between the primary radiation and atomic nuclei; further, the intensity of cosmic radiation might have been much greater in the past, as the super-novae theory of W. Baade and F. Zwicky[5] suggests, so that it would be premature to attempt any quantitative estimate. It is further possible that cosmic ray particles might besides the production of protons, α-particles and + and − electrons, propel the nuclei of heavier elements (like O, Si, Fe and Zr, etc.) and induce them to take part in nuclear reactions. If our assumption is correct, we have to expect also other "*cosmic radio-elements*," so that the total radioactivity in rocks on the surface of the earth would be greater than the sum of the U- and Th-activity and of their disintegration products (with due regard to phenomena of leaching infiltration, etc.).

A complete description of our procedure will be published in due course. Further experimental investigations are highly necessary; for the time being, we are prevented from taking part in them, for we have lately resumed our work on the chemistry of concentrated protactinium preparations.

Sample lot	Method of chemical concn.	Sample, g.	Final concentrate, mg.	Unknown activity per g. of eudyalite	Blanks	Multiple of equilibrium amount $(=N)$
I	I	1000	3	$\simeq 1.4 \cdot 10^{-2}$ mg. U_3O_8	$< 0.3 \cdot 10^{2}$ mg. U_3O_8	$13 \times N$
II	II	100	700	$5.0 \cdot 10^{2}\ \alpha/h$	$< 1.0 \cdot 10^{2}\ \alpha/h$	$8 \times N$
II	III	50	500	$5.0 \cdot 10^{2}\ \alpha/h$	$< 1.0 \cdot 10^{2}\ \alpha/h$	$8 \times N$

The average life of our α-activity is above one year and as its maximum limit a period of 10^6 years can be deduced from the fact that no lines of element 91 were found in the x-ray spectrogram of our 3 mg. concentrate (sample I).

We wish to express our appreciation to I. and W. Noddack (Berlin) for valuable discussions and their many x-ray analyses of our preparations, to V. M. Goldschmidt (Göttingen) and O. B. Böggild (Kopenhagen) for the mineral samples,

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(4) Lord Rayleigh (R. J. Strutt), *Proc. Roy. Soc.* (London), **A80**, 572 (1908).

(5) W. Baade and F. Zwicky, *Proc. Nat. Acad. Sci.*, **20**, 259 (1934).

to R. Evans (Berkeley, Cal.) for the radium determinations and to A. H. Compton and J. Dempster for the privilege of using the facilities of the Dept. of Physics.

KENT CHEMICAL LABORATORY
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CHICAGO, ILL.

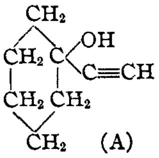
RECEIVED JULY 5, 1934

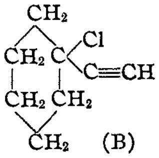
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

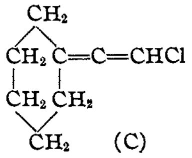
Experiments with Ethynylcyclohexanol and Related Compounds

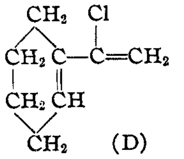
BY CHARLES D. HURD AND RALPH N. JONES[1]

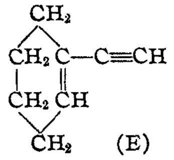
It was of interest to decide whether the product formed by the interaction of chlorinating agents on 1-ethynyl-1-cyclohexanol (A) was 1-ethynyl-1-chlorocyclohexane (B), or cyclohexylidenevinyl chloride (C), or 1-α-chlorovinyl-1-cyclohexene (D).


(A)


(B)


(C)


(D)


(E)

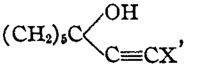
Structure (B) was eliminated since it should have displayed acetylene reactions and possessed a reactive chlorine atom, neither of which it did. To decide between structures (C) and (D) the product was ozonized. Acids would result from either structure but (C) alone should give rise to cyclohexanone. Since cyclohexanone was not found, structure (C) was eliminated and (D) alone remained for consideration. It is true that cyclohexanone does change in part into adipic acid by ozonization[2] but in our work an excess of ozone was purposely avoided. Therefore, the non-detection of cyclohexanone must bear witness to its non-production.

Carothers and Coffman[3] prepared compound (D) by the addition of hydrochloric acid to 1-ethynyl-1-cyclohexene (E) in the presence of cuprous and ammonium chlorides. That their "chloro-2-tetramethylene-3,4-butadiene-1,3" was identical to our compound (D) was confirmed by the following data.

	C. and C.	H. and J.
B. p., °C............	55–57 (1 mm.)	89–92 (21 mm.)
n^{20}_{D}..................	1.5240	1.5230
M. p. of derivative with naphthoquinone....	191–192° (copper block)	185–187° (capillary tube)

Presumably (E) was an intermediate in the transformation of (A) to (D). Some of this enyne (E) was present in the reaction products. Whether the change from (A) into (E) is direct or via (B) cannot be answered.

There were two reasons for considering the allene (C) as a possible reaction product. First, Willemart[4] has postulated, but never isolated, chloroallenes as intermediates in the synthesis of rubrene hydrocarbons from ethynylcarbinols. Secondly, Rupe[5] has reported the transformation of (A) by formic acid into cyclohexylideneacetaldehyde, $(CH_2)_5C{=}CH{-}CHO$. The enol form of this aldehyde, postulated by Rupe as an intermediate, is strictly analogous to (C).

1-Ethyl-1-chlorocyclohexane was prepared normally from 1-ethyl-1-cyclohexanol. This chloride, with a structure analogous to (B), reacted readily with alcoholic potash. 1-Phenyl-1-cyclohexanol was sluggish toward phosphorus pentachloride but the chloride produced was hydrolyzable. In the chlorination (by PCl_5 or $SOCl_2$) of substituted ethynylcyclohexanols,  $(CH_2)_5C\begin{smallmatrix}OH\\ C{\equiv}CX\end{smallmatrix}$, wherein X represents Cl, Br, C_6H_5, there was extensive dehydration to an enyne as well as chlorination.

Experimental Part

Preparation of the Cyclohexanols.—1-Ethyl-1-cyclohexanol,[6] 1-phenyl-1-cyclohexanol,[6] 1-chloroethynyl-1-cyclohexanol[7] and 1-bromoethynyl-1-cyclohexanol[7] were prepared by literature methods. 1-Phenylethynyl-1-cyclohexanol was synthesized by the method of Hurd and Cohen,[8] and since it was not previously characterized, its analysis is given here.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.0. Found: C, 84.0; H, 8.26.

Slight modifications of Rupe's directions[5] were introduced in the synthesis of 1-ethynyl-1-cyclohexanol. In-

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[1] Du Pont Fellow in Chemistry, 1930–1931.

[2] Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 459 (1928).

[3] Carothers and Coffman, THIS JOURNAL, **54**, 4075 (1932).

[4] Willemart, *Compt. rend.*, **187**, 385 (1928).

[5] Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

[6] Sabatier and Mailhe, *Ann. chim.*, [8] **10**, 544 (1907).

[7] Straus, Kollek and Heyn, *Ber.*, **63**, 1868 (1930).

[8] Hurd and Cohen, THIS JOURNAL, **53**, 1074 (1931).