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.

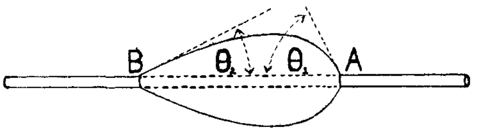


Fig. 1.

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

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-

---

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

[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: $<5.4\cdot10^{-5}$ g. of uranium (x-ray determination, W. Noddack - A. V. Groose); 1.00 g. of eudyalite contains: $1.26\cdot10^{-11}$ g. of radium, corresponding to $3.8\cdot10^{-5}$ 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 = $1.06\cdot10^{-3}$ 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	$\simeq 1.4\cdot10^{-2}$ mg. U_3O_8	$< 0.3\cdot10^{-2}$ mg. U_3O_8	$13 \times N$
II	II	100	700	$5.0\cdot10^2$ α/h	$< 1.0\cdot10^2$ α/h	$8 \times N$
II	III	50	500	$5.0\cdot10^2$ α/h	$< 1.0\cdot10^2$ α/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,

---

[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
UNIVERSITY OF CHICAGO
CHICAGO, ILL.

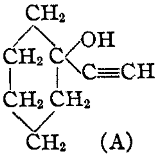
RECEIVED JULY 5, 1934

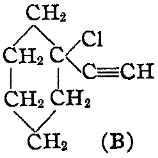
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

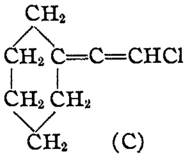
Experiments with Ethynylcyclohexanol and Related Compounds

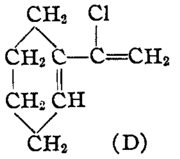
BY CHARLES D. HURD AND RALPH N. JONES[1]

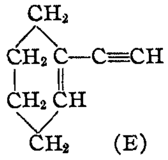
It was of interest to decide whether the product formed by the interaction of chlorinating agents on 1-ethynyl-1-cyclohexanol (A) was 1-ethynyl-1-chlorocyclohexane (B), or cyclohexylidenevinyl chloride (C), or 1-α-chlorovinyl-1-cyclohexene (D). Structure (B) was eliminated since it should have displayed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


(A)


(B)


(C)


(D)


(E)

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_D^{20}	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, $(CH_2)_5C\begin{matrix}\diagup OH\\ \diagdown C{\equiv}CX\end{matrix}$, 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-

---

[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).