Intramolecular Rotation and the Structure of High Polymers. I. The Structure of Polypeptide Chain.

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I. Potential Curve of Internal Rotation. The results of experiments of Raman effect, infra-red absorption, dipole moment and electron diffraction made for ethylene dihalides by Mizushima, Morino, Watanabe, Simanouti, and others[1] in our laboratory have shown that there are three potential minima in one complete rotation about a carbon single bond as axis (see Fig. 1).

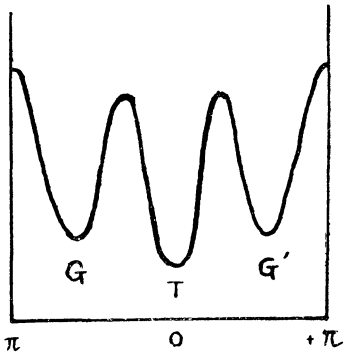


Fig. 1. Potential curve of ethylene dihalide.

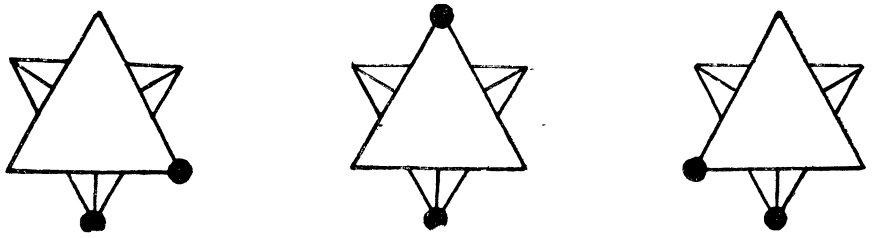


Fig. 2. Molecular forms corresponding to the three potential minima.

These three potential minima correspond to one trans form (T) in which two halogen atoms are at the farthest distance apart and two gauche forms (G and G') obtainable from the trans form by internal rotation

(1) Mizushima, Morino, and others: *Physik. Z.*, 35 (1934), 905; 38 (1937), 459; *J. Chem. Phys.*, 9 (1941), 826; Mizushima, Morino, Watanabe, Simanouti, and others; *Sci. Pap. I.P.C.R.* (Tokyo), 39 (1942), 396, 401; 40 (1942), 87, 100, 417, 425; 42 (1944), *Chem.*, 1, 5, 27, 51.

of ±120° (see Fig. 2). The energy difference between the trans and the gauche minima amounts to 1 kcal/mol (1.2 kcal for ethylene dichloride and 1.3 kcal for ethylene dibromide). The height of potential barrier lying between these two kinds of minima amounts to about 10 kcal/mol, which is much smaller than the activation energy of ordinary chemical reactions so that "rotational isomers" of ethylene dihalides cannot be isolated under ordinary conditions. The experimental results obtained in our laboratory for ethylene chlorhydrin, chloral hydrate, normal paraffins,[2] and cyclohexane can also be explained by considering intramolecular potential of similar type.

II. The Basic Structure of Polypeptide Chain. As a stable configuration of polypeptide chain an extended form (Fig. 3) has already been proposed[3] which corresponds to the structure of silk fibroin or of β-keratin. However, from our experimental results stated in I we can propose another stable chain configuration (bent form) shown in Fig. 4. These two forms do not differ much from each other in internal energy and the bent form may be the more stable of the two because of the existence of intramolecular hydrogen bond (denoted by the dotted lines in Fig. 4).

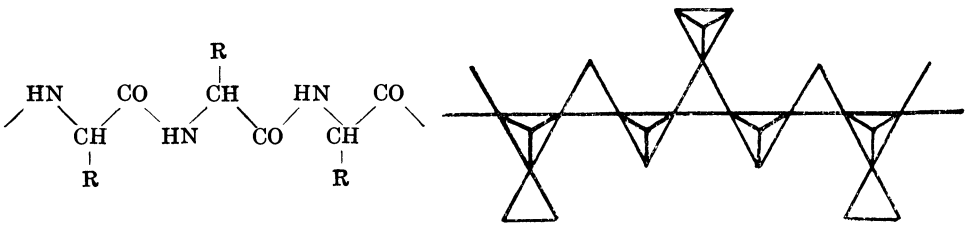


Fig. 3. Extended form.

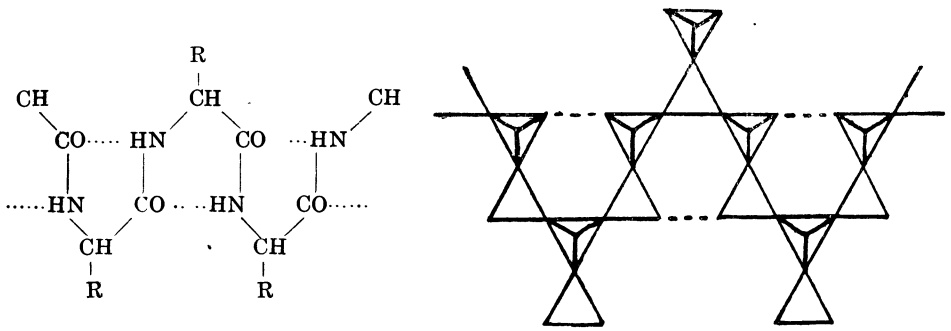


Fig. 4. Bent from.

Other stable forms are obtained by the suitable combination of these two basic structurs. Let us denote the unit structures of the extended

(2) Mizushima and Simanouti: *Proc. Imp. Acad. Tokyo*, 20 (1944), 86. The other results will be published before long.

(3) Meyer-Mark: *Hochpolymere Chemie* II, (1940).

and the bent forms by E and B respectively and hence represent the chain form of Fig. 3 by EEE ---- and that of Fig. 4 by BBB -----. Other conceivable structures are then denoted by EBEB ----, EEBEEB ----, EEEBEEEB ----, etc., among which the ring structures $(EB)_3$, $(EEEB)_3$, $(EBBB)_3$, etc. characterized by trigonal symmetry are included. Let us try to explain the experimental data obtained for proteins by these structures.

1) From the bond radii the period along the chain is calculated as 5.1 A for BBB ---- and as 10.2 A for BBEBBE -----. The experiment of Astbury made for keratin can be explained by these predicted values.[4] The mechanical properties of keratin fiber can also be accounted for by these structures as shown in next section.

2) The X-ray investigations show that the crystal structure of insulin,[5] excelsin,[6] etc. has trigonal symmetry. This is readily understood, if we consider that the molecule of such proteins is made of the said ring such as $(EEE ---- B)_3$, or by the suitable superposition of these plane forms. (The superposition may be caused through the hydrogen bond or the covalency of side chain).

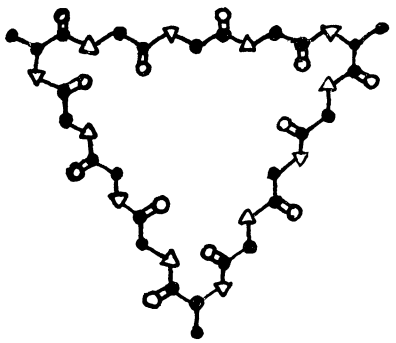


Fig. 5. The trigonal structure $(EEEB)_3$.

3) Whether an amino acid residue in the polypepetide chain takes E-form or B-form depends upon the nature of this residue. In the case of glycine residue which has no side chain E-form can be considered to be the more stable. This is compatible with the fact that silk fibroin molecule containing considerable number of glycine residues has a structure of β-keratin type or EEEEE -----.

In the case of a residue with the side chain which exerts large steric effect to the main chain or which strengthen the intramolecular hydrogen bond (denoted by the dotted line of Fig. 4), B-form becomes the more stable.

4) In any case these two forms E and B do not differ much in

(4) Astbury and Street: *Phil. Trans. Roy. Soc.* (London), A 230 (1931), 75.
(5) Crowfoot: *Proc. Roy. Soc.* (London), A 164 (1938), 580.
(6) Astbury, Dickinson, and Baily: *Biochem. J.*, 24 (1935), 2351.

their energy and the polypeptide chain tends to change its configuration by a slight change in the external condition. We can thus understand why some proteins are denatured easily and also why some proteins such as antibodies show quite specific properties.

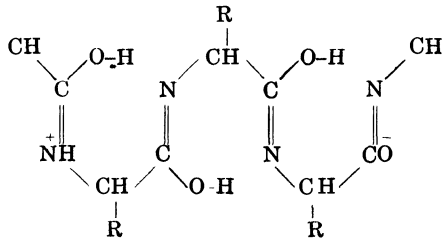


Fig. 6.

5) For BBB ---- structure a resonance form shown in Fig. 6 can be considered. This means that in some case the polypeptide chain may form an extended oscillator just as a molecular chain with conjugated double bond and thus we may explain by a field of forces resulting from this oscillator the mechanism of the combination of dyes with proteins, etc.

III. The Structure of α-keratin. No satisfactory explanation for the structure of α-keratin has hitherto been advanced. However, we consider that BBB ---- or BBEBBE ---- can represent this structure by which we can explain reasonably the experimental data obtained for α-keratin as follows:

1) The period along the fiber axis observed for α-keratin amounts to 5.15 A, which is in good agreement with that predicted from the structure BBB ----. The side chain spacing is found to be 9.8 A in β-keratin as well as in α-keratin. This is comprehensible, if we consider that cystine bond remains unchanged in both keratins (see Fig. 7 and 8).

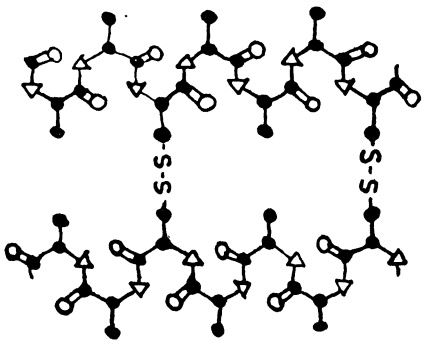


Fig. 7. Cystine bond in α-keratin.

The backbone spacing 4.65 A of β-keratin is not found in α-keratin. This will be due to the disconnection of intermolecular hydrogen bond of β-keratin which in turn forms the intramolecular hydrogen bond of

α-keratin denoted by the dotted lines of Fig. 4.

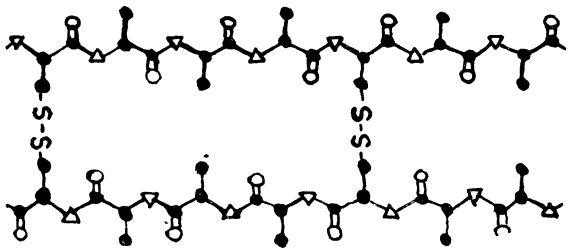


Fig. 8. Cystine bond in β-keratin.

The supercontraction of wool may also be explained, if, for example, we consider a structure such as shown in Fig. 9, which can be obtained by the disconnection of cystine chain.

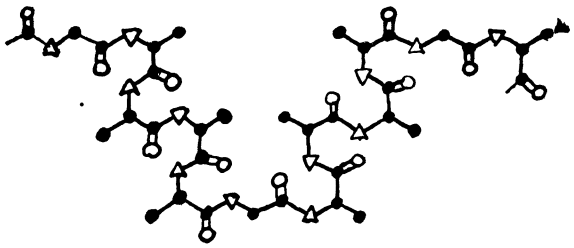


Fig. 9. An example of the structure of supercontracted wool.

2) Let us next discuss the mechanical properties of wool. For an elongation Δl within 2% Hooke's law is found to hold. We have, therefore,

$$E = \frac{1}{2}k(\Delta l)^2 \tag{1}$$

where E is the change in energy and k the force constant. Let y be Young's modulus refered to a single molecule and l_0 be an equilibrium length of an amino acid residue along the chain. Then y is defined as:

$$y = \frac{\partial E}{\partial \Delta l} \Big/ \frac{\Delta l}{l_0} \tag{2}$$

From Eq. (1) and (2) we have

$$y = kl_0 \tag{3}$$

The value of Young's modulus Y in its ordinary sense can be obtained from the experimental relation[7] between the tension K and the elongation $\Delta L/L_0$:

(7) Astbury and Coworkers: *Phil. Trans. Roy. Soc.* (London), A 230 (1931), 75; 232 (1933), 333; *Trans. Farad. Soc.*, 29 (1933), 193; *Proc. Roy. Soc.* (London), A 150 (1935), 533.

$$Y = K \Big/ \frac{\Delta L}{L_0} = \frac{10 \times 10^5}{0.02} = 5 \times 10^7 \text{ g/cm}^2 \qquad (4)$$

We can now put

$$\frac{\Delta l}{l_0} = \frac{\Delta L}{L_0}$$

$$y = YA ,$$

where A denotes the molecular cross section. This can be calculated from the observed side chain spacing 9.8 A of α-keratin and the backbone spacing which is assumed reasonably to be 6 A. We have then

$$k = \frac{y}{l_0} = \frac{YA}{l_0} = \frac{(5 \times 10^7 \times 980)(9.8 \times 6 \times 10^{-16})}{2.57 \times 10^{-8}} = 1.1 \times 10^4 \text{ dyne/cm} \qquad (5)$$

This value of k is found quite reasonable when compared with the force constant of hydrogen bond.[8)]

Let us next discuss larger elongation. The X-ray diagram shows that in this case the structure of α-keratin changes into that of β-keratin. Let E_2 be the energy of E-form refered to B-form, l_1 and l_2 be the length of an amino acid residue in B- and E-forms, and n_1 and n_2 be the number of residues in B- and E-forms, respectively, we have for the length L and energy E of a polypeptide chain

$$L = n_1 l_1 + n_2 l_2 = n l_1 + n_2 (l_2 - l_1) \qquad (6)$$

$$E = n_2 E_2 \qquad (7)$$

where $n = n_1 + n_2$

In the case of the coexistence of both forms the tension per unit chain K is calculated as

$$KA = \frac{\partial E}{\partial L} = \frac{\partial E}{\partial n_2} \frac{\partial n_2}{\partial L} = \frac{E_2}{l_2 - l_1} \qquad (8)$$

From this relation we see that all B-forms change into E-forms for a certain value of tension, at which the tension-elongation curve becomes parallel to the elongation axis. That such is not actually the case is due to the neglection of entropy in the foregoing discussion. The value of entropy will be very small in both extreme cases where all amino acid residues take B- or E-form, but in the intermediate case its value will be considerable, so that the said curve inclines to the elongation axis to some extent. If we put the value of tension 6×10^5 g/cm^2 (corresponding to the middle point of the slope of tension-elongation curve observed in

(8) Halford: *J. Chem. Phys.*, 14 (1946), 395.

the measurement for the relative humidity of 100%) into K of Eq. (8) and put

$$l_2-l_1 = 3.32-\frac{5.14}{2} = 0.75\,\text{A}\,,$$

we can calculate the energy difference between B- and E-forms as:

$$E_2 = 370\ \text{cal/mol}$$

The structure of α-keratin may also be considered as BBEBBE ----[9] (see Fig. 10), for which the period along the main chain is calculated as 10.3 A. This is also compatible with the experiment.[10]

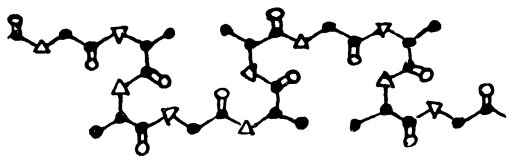


Fig. 10. α-keratin.

In this case the side chain (cystine bond) is directed upwards or downwards from the plane of Fig. 10, and therefore, the corresponding spacing (9.8 A) remains constant, when the chain is stretched out. If, therefore, we assume the backbone spacing as 9 A, we can calculate the force constant k and the energy difference E_2 just as in Eq. (5) and (8):

$$k = \frac{(5\times10^7\times980)(9.8\times9\times10^{-16})}{5.15\times10^{-8}} = 0.84\times10^4\ \text{dyne/cm},$$

$$E_2 = KA(l_2-l_1) = 1800\ \text{cal/mol (residue)}.$$

The elongation of wool will not be explained by a single mechanism, as the experiment of Bull[11] shows. (The electron microscope experiment[12] shows that keratin fiber has specific fine structure, and, therefore, it may consist of complex micelles.) Hence the foregoing discussion will not cover all the elongation steps. However, since X-ray diagram shows the structural change (α to β change) after elongation, it will be difficult to explain the mechanical property of keratin fiber without taking into account the intramolecular rotation as stated above.

(9) This can be considered as a structure in the state of supercontraction, if the structure of keratin fiber in its ordinary state is represented by the configuration shown in Fig. 4.

(10) The intensity relation of X-ray scattering may more reasonably be explained by the structure of Fig. 10 than that shown in Fig 4. We are indebted to Dr. N. Tanaka for the discussion on this structure.

(11) Bull: *J. Am. Chem. Soc.*, **66** (1944), 1253; **67** (1945), 533.

(12) Mercer: *Nature*, **159** (1947), 535. See also Bear: *J. Am. Chem. Soc.*, **65** (1943)' 1784; **66** (1944), 2043.

The discussion of globular proteins based on the structure proposed by us will be given in a later communication.

Faculty of Science and Radiation Chemistry Research Institute, Tokyo University.

Études spectrochimiques des complexes métalliques renfermant la molécule triazène. I[1]. Sur les triazènes dinitrés.

Par Taku UÉMURA, Yasuhisa SATO et Shun-ichi ARIKAWA.

(Reçu le 6 juillet 1948.)

Introduction. Plusieurs auteurs, comme R. Meldola,[2] O. Dimroth,[3] F. M. Perkin[4] et A. Mangini,[5] ont déjà observé les sels métalliques des amines secondaires et ils ont fait la méthylation pour savoir quel azote du triazène a la fonction de l'amine secondaire. Ils les ont décomposés et ont essayé de tirer la structure chimique de ces produits décomposés, mais ils n'ont pas réussi d'obtenir les résultats satisfaisants. W. Watt[6] et F. P. Dwyer[7] et son collaborator ont encore minutieusement étudié les mêmes matières et surtout Dwyer publiait une étude sur la constitution de "chelation" d'anneau des quatre membres. Les présents auteurs ont mesuré les spectres d'absorption de triazène et ses dérivés métalliques pour éclairer la struture chimique et le caractère salifiable par leurs études spectroscopiques. Ils ont d'abord pris le triazène (C_6H_5-N=N-NH-C_6H_5, benzène-diazo-aminobenzène ou diazoamidobenzol), corps fondamantal, et ses dérivés dinitrés pour en rendre compte dans le présent mémoire. Ils ont encore l'intention de continuer leurs recherches sur les sels complexes métalliques conduits des composés ci-dessous indiqués.

Synthèse des échantillons. Les échantillons que nous avons employés pour nos études ont été tous préparés par les méthodes déjà connues. Nous avons utilisé le dinitro-triazène que nous avons obtenu avec la nitraniline purifiée par les recristallisations répétées d'alcool et d'eau chaude. Le point de fusion de ces nitranilines que nous avons employées se présentent respectivement 147° pour le para-composé, 72° pour l'ortho- et 112° pour le méta-. Le dinitro-triazène synthétisé a été encore purifié par plusieurs recristallisations de l'alcool (Table 1). Les corps obtenus sont généralement des cristallines fines et celles de 3.3'-dinitro-triazène étaient comme une masse de coton constituée par de petits cristaux aiguillés.

(1) Exposé fait lors de la 68e Séance annuelle de la Société chimique du Japon, octobre 1946.

(2) R. Meldola et F. W. Streatfeild, *J. Chem. Soc.*, **49** (1886), 624; **50** (1887), **102**, 434; **51** (1888), 664.

(3) O. Dimroth, *Ber.*, **40** (1907), 2390.

(4) F.M. Perkin, *Ber.*, **30** (1897), 1394.

(5) A. Mangini, *J. Soc. Chem. Ind.*, **58** (1939), 327.

(6) W. Watt, *Z. anorg. allgem. Chem.*, **221** (1935), 187.

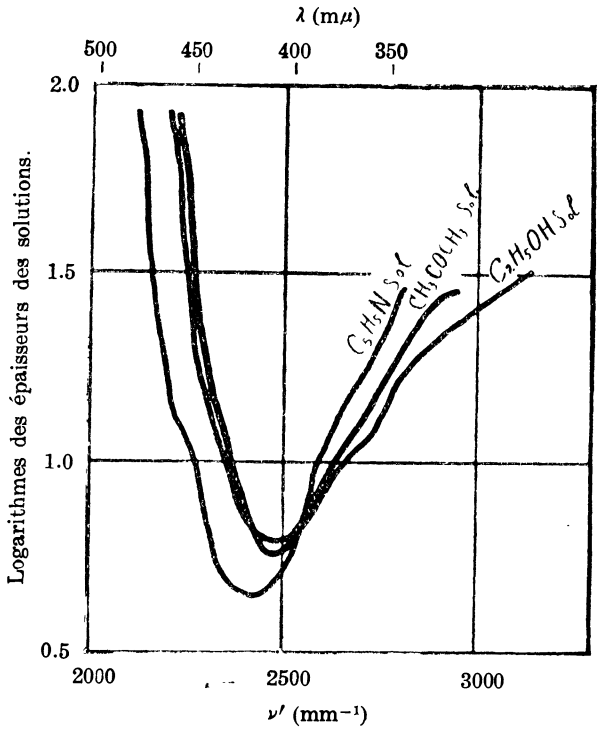
(7) F.P. Dwyer, *J. Soc. Chem. Ind.*, **56** (1937), 70; **57** (1938), 351, 357; **58** (1939), 110; *J. Am. Chem. Soc.*, **63** (1941), 78; F. P. Dwyer et D.P. Mellor, *J. Am. Chem. Soc.*, **63** (1941), 81.

Table 1.

Dinitro-triazène	4,4′—	2,2′—	3,3′—	4,2′—	2,4′—	4,3′—	3,4′—	2,3′—	3,2′—
Point de fusion (C°) (Décomposition)	221°	198°	194°	193°	192°	222°	223°	171°	170°
Couleur	jaune	jaune	jaunâtre	jaune orangé	jaune orangé	jaune	jaune	jaune	jaune

F. P. Dwyer[7] a observé qu'il y a deux types (jaune et orangé ou rouge violet) dans les dinitro-triazènes, excepté le 3,3′-composé, et il a réussi à séparer les deux types de 4,4′- et 2,2′ composés aux quels il a donné les noms: "type normal" à modification jaune, "type aci" à modification rouge. D'autre part, A. Mangini[5] a attribué ces deux modes aux isoméries géométriques cis- et trans-. Nous avons seulement pris les échantillons synthétisés recristallisés de l'alcool pour photographier les spectres et nous n'avons essayé aucune séparation du composé que Dwyer a nommé "original". Nous croyons que ces deux modifications contiennent en quantité équivalente dans nos corps préparés et nos études spectrochimiques nous ont confirmé notre supposition, c'est-à-dire, nous n'avons pas pu trouver l'absorption caractéristique de ces deux types.

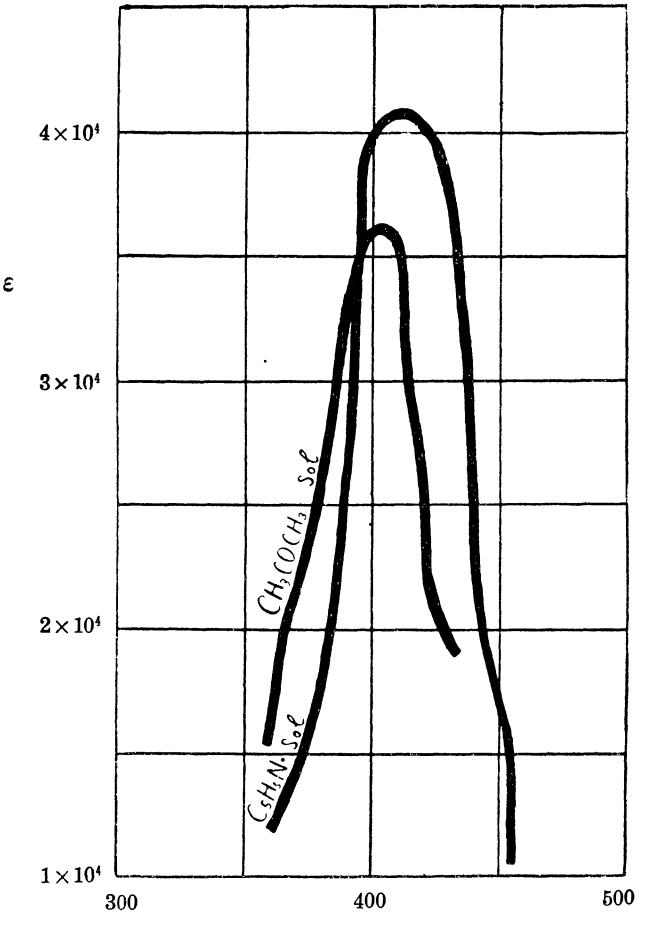
Influences des dissolvants. Le triazène et le dinitro-triazène sont peu solubles dans l'eau et le benzène, bien solubles dans le phénol, l'acétone et



4,4′-Dinitro-triazène.

Fig. 1.

la pyridine. La Fig. 1 expose qualitativement les spectres d'absorption du 4,4'-dinitro-triazène dissous dans l'alcool, l'acétone et la pyridine. La solution alcoolique et celle d'acétone donnent à peu près le même résultat tandis que la solution pyridique montre une courbe un peu différente. On a quantitativement mesuré en employant l'acétone et la pyridine comme ses dissolvants (Fig. 2).



4,4'-Dinitro-triazène.

Fig. 2.

La solution pyridique nous a donné ses spectres d'absorption bathochromiques ayant un grand pouvoir absorbant, et l'acétone qui a l'absorption semblable à celle de l'alcool, était choisie comme échantillon, car la première est plus soluble que le second. La pyridine et l'acétone ont leurs absorptions dans la région des longueurs d'onde plus courtes que 330 mμ. Comme leur principale bande d'absorption se trouve cependant dans la

région visible ou son voisinage ultraviolet, ces deux dissolvants peuvent être adopter.

Relation entre la position du radical nitré et l'absorption du rayon lumineux. Les spectres d'absorption du diazoamidobenzol (triazène) ont été comparés avec ceux de ce composé dinitré pour savoir les effets de la position du radical nitré.

La Fig. 3 montre les courbes d'absorption des solutions acétoniques de six triazènes dinitrés (4,4′-, 2,2′-, 3,3′-, 4,2′-, 4,3′-, et 2,3′-), et la Fig. 4, celles des solutions pyridiques des mêmes composés ci-dessus nommés.

Nous en avons observé le pouvoir absorbant maximum (ε max) et

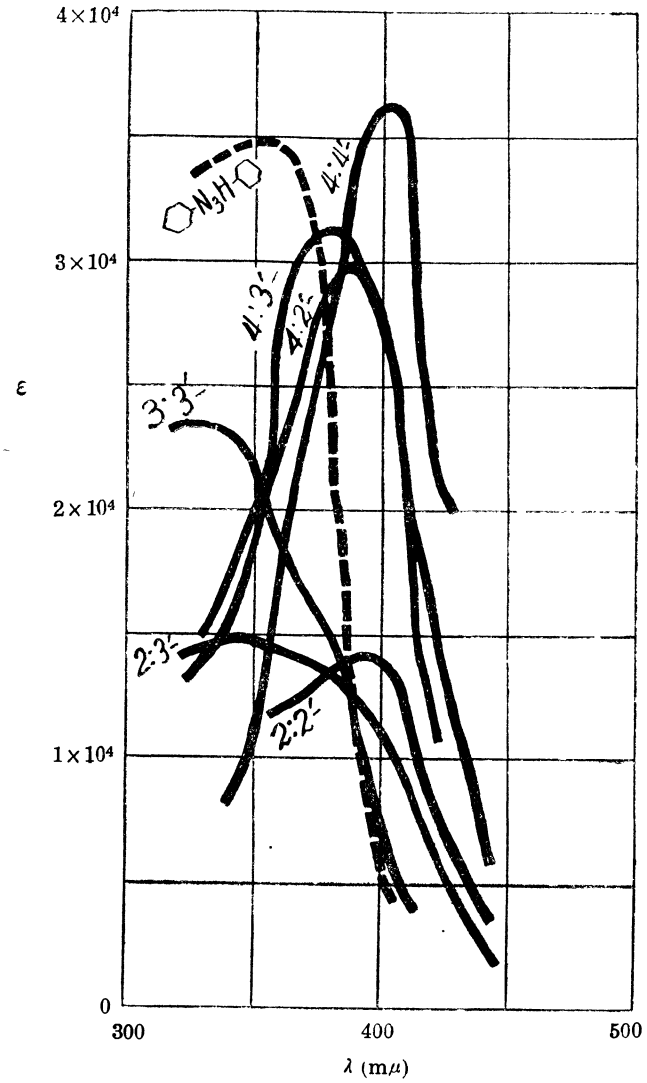


Fig. 3. Triazène et dinitro-triazènes (solutions acétoniques).

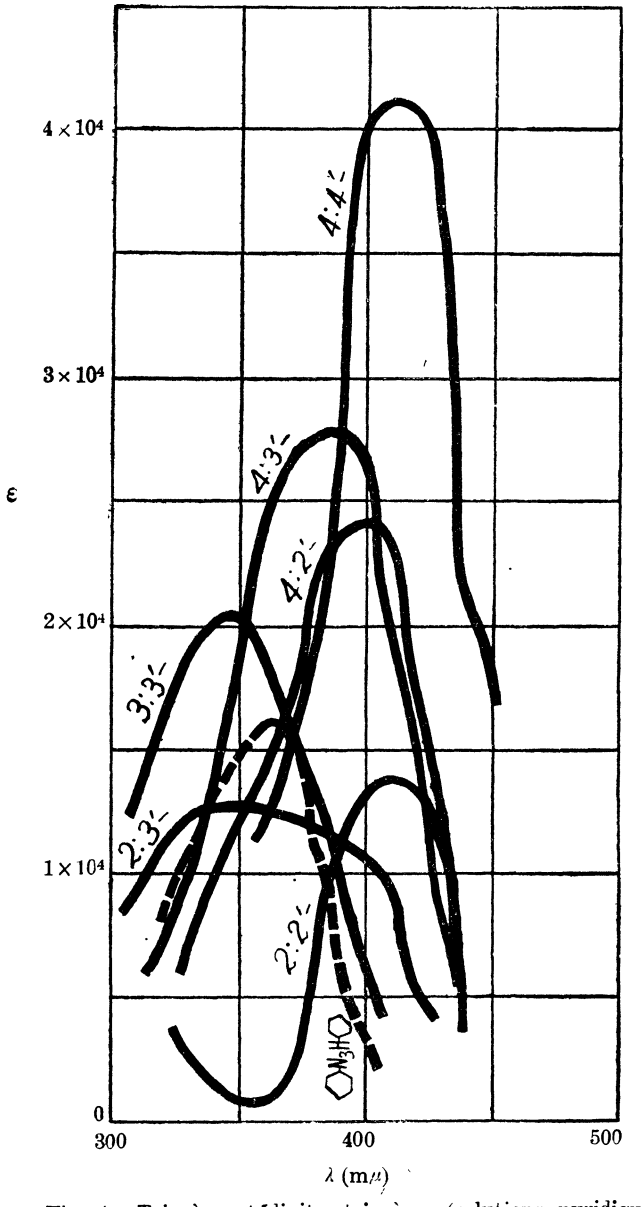


Fig. 4. Triazène et dinitro-triazènes (solutions pyridiques).

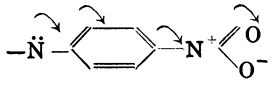
la longueur d'onde maximum correspondante (λ max) que nous avons donnés dans la Table 2.

Quand le radical nitré entre la para-position ou l'ortho-position envers le radical diazoaminé, la bande d'absorption change vers des longueurs d'onde plus élevées. Ces effets bathochromiques ont probablement apparu par la transformation du type benzénique en celui de quinone (quinonique). Le radical nitré renferme généralement la liaison de son π-type, et comme la structure de résonance comparablement stable est toujours possible

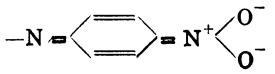
Table 2.

	Solutions acétoniques		Solutions pyridiques	
	λ max. (mμ)	ε max. (×10⁴)	λ max. (mμ)	ε max. (×10⁴)
Triazène	350	3.48	364	1.60
4,4′-dinito-triazène	401	3.62	412	4.09
2,2′-dinitro-	397	1.46	410	1.38
3,3′-dinitro-	environ 330	2.38	347	2.03
4,2′-dinitro-	386	3.00	398	2.42
4,3′-dinitro-	378	3.15	388	2.78
2,3′-dinitro-	environ 345	1.50	350	1.28

d'exister, la paire électronique ayant la propriété additive doit être donnée à l'atome d'azote. C'est pour cela, au cas du para-composé, qu'une paire électronique partie de l'azote aminé (a), passe par le nucléus benzénique et produit la structure quinonique polaire et typique (b).

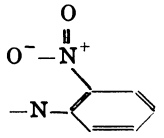


(a)

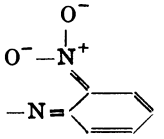


(b)

On peut appliquer la même déduction au composé ortho-nitré et le type ortho-quinonique peut se trouver (a′ et b′).

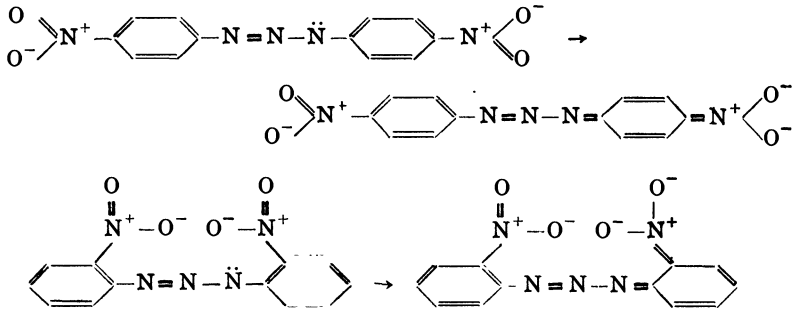


(a′)



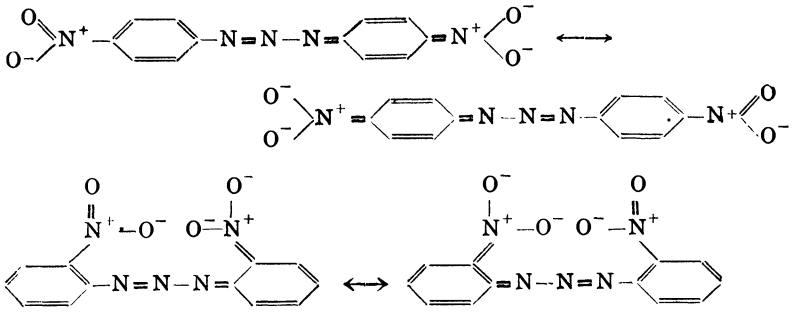
(b′)

La constitution quinonique, ortho- et para-, peuvent aussi exister dans les produits substitués du triazène indiqués ci-dessous.



Cette transformation explique que les doubles liaisons conjuguées se produisent entre les deux radicaux nitrés dans les composés, ortho- et para-, en montrant la constitution polaire. On peut trouver en même temps que le para-composé prend plus facilement la structure symétrique que l'ortho-. Le moment bipolaire du para-composé peut aussi bien augmenter que celui du ortho- et sa variation est naturellement grande et

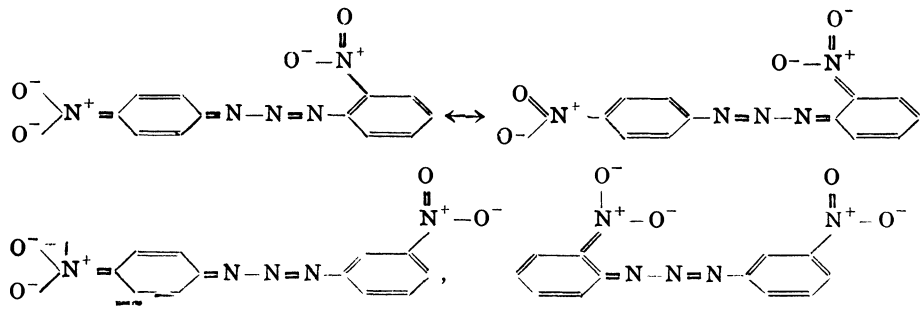
son absorption devient plus bathochromique. C'est encore possible de supposer que la constitution quinonique des composés, ortho- et para-, peut prendre encore celle de résonance.



Les ortho-composés ne montrent qu'un pouvoir absorbant considérablement faible et c'est peut-être l'action mutuelle entre les radicaux nitré et aminé qui empêchent la résonance, mais, dans ce cas, il serait possible de constituer la combinaison -O-H-N-.

Pour les méta-composés, on observe que leur bande d'absorption a la tendence de devenir un peu vague, leur pouvoir absorbant n'est pas remarquable et plutôt hypsochromique le comparant avec le triazène non-nitré. Cela explique qu'il est presque impossible de transformer ces méta-composés au type quinonique polaire; par conséquent, les doubles liaisons conjuguées sont coupées et la structure de résonance stable ne peut pas être manifestée.

Quant aux composés nitrés asymétriques, on peut déduire de pareilles conclusions déjà données aux dinitro-triazènes symétriques, et les confirmer par les résultats obtenus des spectres d'absorption, c'est-à-dire, les composés comme 4,2′- et 4,3′- qui ont un radical nitré à la para-position, sont bathochromiques en montrant fortement l'effet du radical, tandis que, dans le 2,3′-composé, les propriétés appartenant aux ortho- et méta-composés, comme le faible pouvoir absorbant et la bande d'absorption diffusée, peuvent être superposées. Quand un radical nitré entre à la méta-position dans un nucléus benzénique, la constitution de résonance stable n'existe pas par les raisons ci-dessus décrites.



La bande d'absorption de la solution pyridique est plus faible que

celle donnée par la solution acétonique, mais cette absorption manifeste l'effet bathochromique assez fort, c'est-à-dire, le triazène et ses dérivés 3,3′- et 2,3′-dinitrés donnent une bande d'absorption plus claire en solution pyridique que celle donnée par leur solution acétonique qui est assez large. Dans ce cas, le pouvoir absorbant est aussi influencé un peu différemment de la solution pyridique.

Sur les composés dinitrés ayant les radicaux nitrés dans les positions asymétriques. Nous avons préparé les composés dinitrés ayant leurs radicaux nitrés dans les positions 2,4′-, 3,4′- et 3,2′- qui sont respectivement les paires sur les positions 4,2′-, 4,3′- et 2,3′-. Avec ces trois paires des dérivés synthétisés, l'identité de ces trois est respectivement confirmée par leur absorptions lumineuses et le "mischprobe". (Table 3.)

Table 3.

Radicaux nitrés	4,2′—	2,4′—	4,3′—	3,4′—	2,3′—	3,2′—
Point de fusion	193°	192°	222°	223°	171°	170°
"mischprobe"	191°		221°		170°	

On comprendra cette confirmation par la courbe d'absorption de

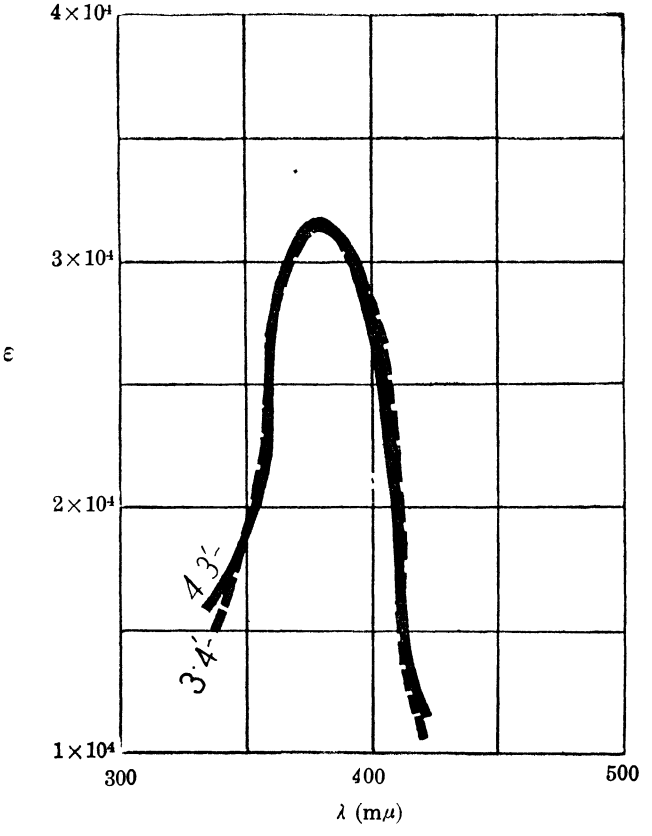
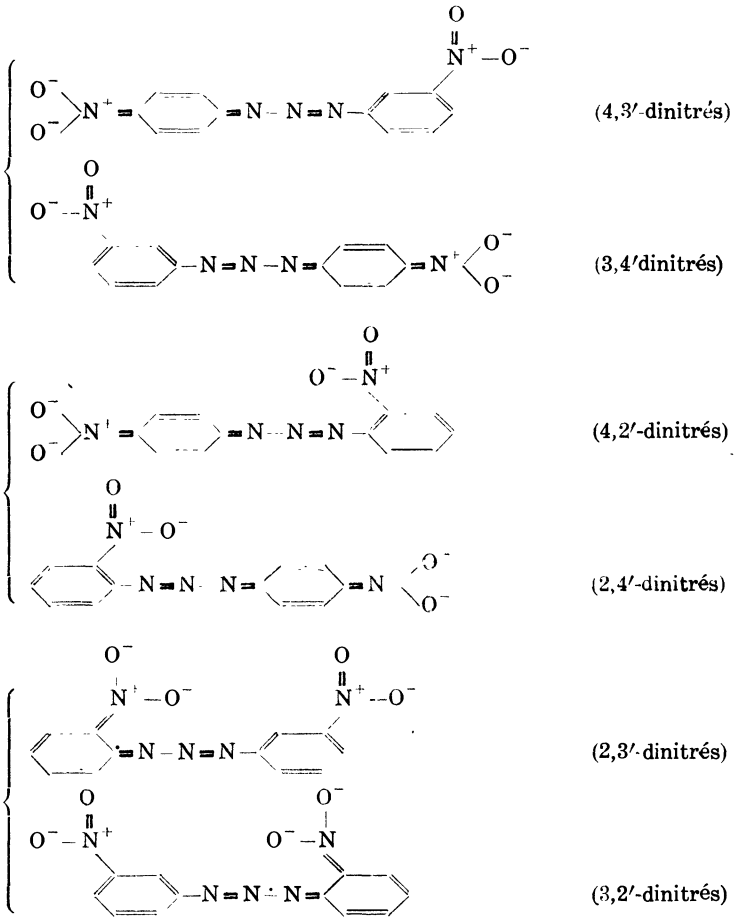


Fig. 5. 4,3′- et 3,4′-Dinitro-triazènes (solutions acétoniques).

l'exemple de Fig. 5 où l'on a pris les deux triazènes 4,3′- et 3,4′-dinitrés dissous dans l'acétone.

Ces expériences nous montrent que les radicaux nitrés asymétriquement entrés des trois paires donnent essentiellement peu de différences aux résultats qui nous présentent une base forte pour déterminer leur constitution chimique.[8]



Résumé. (1) Nous avons préparé le triazène et ses dérivés dinitrés pour mesurer leurs absorptions lumineuses. Nous avons observé que leur principale bande d'absorption se trouve dans la région visible et son voisinage ultraviolet. Ces absorptions sont à peu prés semblables en solutions alcooliques et acétoniques, mais un peu différentes en solutions pyridiques.

(2) Nous n'avons pas constaté d'absorption caractéristique correspondante aux deux modes qu'on appelle "type jaune" et "type rouge".

(8) Meldola a prouvé l'identité des isomères par ses produits de la décomposition[9].

(3) Nous avons désigné au para- composé la structure quinonique stable et polaire qui peut montrer un pouvoir absorbant fort et bathochromique et la résonance.

(4) Nous pouvons supposer que le petit pouvoir absorbant du l'ortho-composé est probablement dû à une action mutuelle entre les radicaux nitré et aminé en affaiblissant la résonance.

(5) Le méta-composé ne manifeste ni effet bathochromique, ni pouvoir absorbant considrérable. Nous en concluons que cette structure ne peut ni se transformer en type quinonique polare, ni présenter de constitution de résonance assez stable.

(6) Nous comprenons que les bandes d'absorption des dérivés nitrés asymétriques donnent les effets superposés appartenant à chaque radical.

(7) Nous avons trouvé que les trois paires de dinitro-triazène asymétriquement nitrés sont identiques par les résultats confirmés par le "mischprobe" et l'absorption lumineuse.

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On the Color Reaction Between Iodine and the Basic Acetates of Some Rare Earth Elements.

By Kenjiro KIMURA and Nagao IKEDA.

(Received July 6, 1948.)

It was found by Damour[1] that basic lanthanum acetate acting with iodine shows a blue color which resembles to that produced by the familiar iodine-starch reaction. Biltz,[2] Berczeller,[3] Lottermoser and Herrmann,[4] Krüger and Tschirch,[5] etc. observed the same phenomenon.

As for the action of iodine upon the basic acetates of rare earth elements other than lanthanum, there are also some reports published.[6] Although Orlow[7] noticed the similar reaction in the case of basic praseodymium acetate, it is generally believed that the above-mentioned color reaction is specific to lanthanum.[8] But, according to the present authors' experiments, besides the basic acetate of lanthanum, those of praseodymium, neodymium and samarium take on an intense indigo color when properly treated with iodine, while those of yttrium, gadolinium and erbium remain colorless with the same treatment.

Materials. The purity of the salts of the rare earth elements used was examined by the X-ray spectroscopic method. As for lanthanum, praseodymium, neodymium, samarium and gadolinium, the amount of impurities was so small that they might be assumed for the present purposes to be sufficiently and highly pure. Compared with the above-mentioned salts, the purity of yttrium salts used was somewhat low, and that of erbium salts used was still lower. The acetates were prepared according to the method of Lottermoser and Herrmann[9] from oxides and acetic acid.

The Color Produced by the Iodine-Basic Acetate Reaction. A solu-

(1) Damour, *Compt. rend.*, 43 (1856), 976.

(2) Biltz, *Ber.*, 37 (1904), 719.

(3) Berczeller, *Biochem. Zt.*, 84 (1917), 160.

(4) Lottermoser, *Kolloid-Zt.*, 33 (1923), 271; Lottermoser u. Herrmann, *Z. physik. Chem.*, 122 (1926), 1.

(5) Krüger u. Tschirch, *Ber.*, 62 (1929), 2776; 63 (1930), 826.

(6) e.g. Damour, *op. cit.*; Behrens, *Chem. CB.*, (1902) I, 296; Orlow, *Chem-Ztg.*, 31 (1907), 45; Krüger u. Tschirch, *op. cit.*

(7) Orlow, *op. cit.*

(8) Krüger and Tschirch (*op. cit.*) described in their first report that basic praseodymium acetate showed the color reaction with iodine, but later they considered that it was due to the impureness of the materials used and, in their second report, withdrew what was stated in their former report.

(9) *op. cit.*

tion of each acetate was treated with ammonia[10] and basic acetate was precipitated. A solution of iodine and potassium iodide was added to it. Being left at room temperature for 2 or 3 days, it took on gradually a color[11] mentioned in the second column of Table 1. But when it was heated about 10 minutes by immersing the vessel in the boiling water, an indigo color developed immediately in the cases of lanthanum, praseodymium, neodymium and samarium as shown in the third column of Table 1. For comparison, the descriptions of Krüger and Tschirch,[12] which are quite different from ours in the cases of praseodymium, neodymium and samanium, are given in the fourth column of Table 1.

Table 1. The Colors of Iodine-Basic Acetates.

Elements	When left at room temperature	When heated in the boiling water	According to Krüger and Tschirch
Yttrium	Colorless	Colorless	Colorless
Lanthanum	Indigo	Indigo	Indigo
Praseodymium	Blue	Indigo	Colorless
Neodymium	Bluish violet	Indigo	Colorless
Samarium	Yellow	Indigo	Colorless
Gadolinium	Colorless	Colorless	—
Erbium	Colorless	Colorless	Colorless

The colored precipitate, after being left 2 days at room temperature and after the removal of free iodine from it, was shaken vigorously with

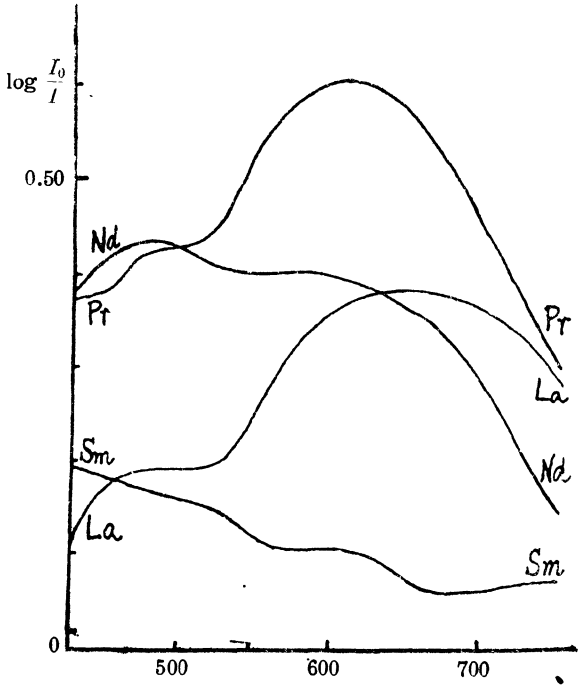

Fig. 1.

water. The water took on the same color as the precipitate. The colored solution thus formed was separated from the precipitate with the aid of a centrifuge and was examined with the Pulfrich photometer. The absorption curves obtained are given in Fig. 1, where I_0 denotes the intensity of the initial light and I, that of the light transmitted.

It is seen from the figure that the absorption maximum of lanthanum salt lies in the longest wave-length side, and those of the salts of the other elements shift to the shorter wave-length side in the order of praseodymium, neodymium and samarium. The absorption maximum of samarium salt does not appear in the visible part.

From this fact, it may be allowed to conclude that the absorption maximum of the iodine-basic acetate color shifts to the shorter wave-length side with the increase of the atomic numbers of the rare earth elements, i.e. with the decrease of the basicity of the elements. The colorlessness of the iodine-basic acetates of gadolinium, erbium and yttrium, which was shown in the experiments, may also be expected from this rule.

The Change of Color with the Lapse of Time. As Berczeller[13] and Lottermoser[14] already pointed out, the color of iodine-basic lanthanum acetate changes from reddish brown or brown to blue with the lapse of time. We studied the color change with the Pulfrich photometer. The experimental procedure was as follows.

To 1 ml. of lanthanum acetate solution[15] were added 0.3 ml. of 1N. ammonia and 2 ml. of 0.1N. iodine-potassium iodide solution. The mixture after being left at room temperature for a definite time mentioned in Fig. 2, was treated in the same way as already mentioned; thus the solution for the photometric measurement was prepared. The absorption curves obtained are given in Fig. 2.

From this figure, it would be seen that the absorption maximum shifts to the longer wave-length side with the lapse of time,[17] and that

(10) The color did not appear when a large excess of ammonia was used; so such large excess of it should be avoided. Also the insufficient quantity of it should be avoided, as such insufficient quantity caused the incomplete precipitation of basic acetate.

(11) In order to remove the yellow or brown color due to free iodine, the precipitate after the treatment was washed with water by decantation with the aid of a centrifuge. Then the color was observed.

(12) In stead of acetates, Krüger and Tschirch (*op. cit.*) used the mixture of the nitrates of the rare earth elements and sodium acetate. We also carried out the experiments with the same mixtures as theirs but, contrary to their results, we confirmed that praseodymium, neodymium and samarium showed the above mentioned color reaction.

(13) *op. cit.*

(14) *op. cit.*

(15) 1 ml. of the solution corresponds to 11.5 mg. of La_2O_3.

(16) The room temperature was between 10.4°C and 16.4°C during these experiments. Any particular attentions to keep the temperature constant were not paid.

(17) Immediately after the addition of iodine solution, the basic lanthanum acetate takes on a reddish brown color. After 1 hour, it becomes reddish violet, after 5 hours, violescent indigo and finally it takes on an indigo color.

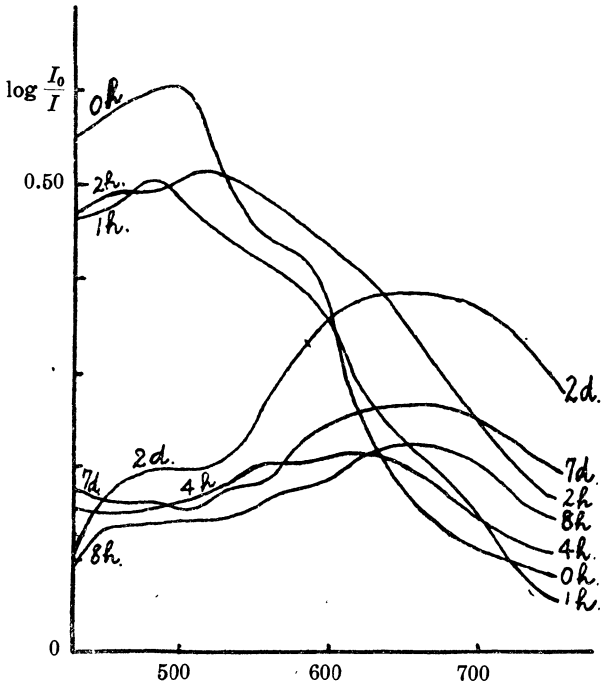

Fig. 2.

the shape of the curve after 8 hours is similar to that after 7 days, in other words, the final indigo color appears already in 8 hours and is stable at least for 7 days.

The similar results were obtained with praseodymium and neodymium, but compared with lanthanum, the color changes somewhat more slowly with these elements.

The Relation between the Concentration of Iodine and the Quantity of Sorbed Iodine. As for the relation between the concentration of iodine and the quantity of sorbed iodine, Lottermoser[18] pointed out that Freundlich's sorption isotherm holds good in the case of basic lanthanum acetate. According to our experiments, it also holds good in the cases of the basic acetates of praseodymium and neodymium.

The Mechanism of the Interference of Other Ions. As for the effect of other ions upon the color of iodine-basic lanthanum acetate, many experimental results were reported by Krüger and others.[19] According to them, the presence of other rare earth elements greatly interfered with the formation of the blue colored substance, but it is not so in our experiments with praseodyminum and neodymium. The mixture of the basic acetates of lanthnum, praseodymium and neodymium also took on an indigo color and no mutual interference was recognized. But the interfering effect of the rare earth elements which did not show the

(18) *op. cit.* (19) *op. cit.*

above-mentioned color reaction was considerable. For example, when yttrium was present in a quantity larger than 0.7:1 in the atomic ratio to lanthanum, no coloration of basic lanthanum acetate was seen.

It is also mentioned in the literature that the interfering effect of fluoride ions, sulfate ions, etc. is remarkable, while that of nitrate ions, chloride ions, etc. is not much. But no satisfactory explanation of the mechanism of the effect of these ions is hitherto given. One possible explanation by the present authors is as follows. When a lanthanum solution containing acetate ions and the interfering ions, e.g. sulfate ions, is treated with ammonia, the basic lanthanum sulfate, which shows no color reaction with iodine, precipitates in earlier stages and interferes with the action of the basic lanthanum acetate which precipitates later. On the contrary, when a lanthanum solution containing acetate ions and the non-interfering ions, e. g. nitrate ions, is treated with ammonia, the precipitation of the basic lanthanum acetate occurs before that of the basic lanthanum nitrate which shows no color reaction with iodine, and the action of basic lanthanum acetate is not greatly interfered. The results of the following experiments seem to support such an interpretation.

(1) A solution containing lanthanum acetate and ammonium sulfate was treated with an insufficient amount of ammonia. The precipitate thus formed showed no color reaction even when it was heated. But the precipitate formed with a sufficient quantity of ammonia took on an indigo color with iodine.

(2) When a solution containing a larger amount of sulfate ions was treated with a sufficient quantity of ammonia, the precipitate thus formed took on only a faint color with iodine. But, even in such a case, if a solution. after the previous removal of the precipitate which was formed with an insufficient amount of ammonia, was treated again with ammonia, the precipitate then formed showed distinctly the color reaction.

(3) When the amount of sulfate was still larger and exceeded the quantity equivalent to lanthanum, no colored precipitate was produced in spite of the presence of acetate ions in the solution. In such a case, the previous removal of the precipitate formed in earlier stages just mentioned above was of no use.

(4) The precipitate, which was formed with a small amount of ammonia from a solution containing lanthanum acetate and lanthanum nitrate, took on an indigo color with iodine. But the precipitate formed with a larger amount of ammonia was only unevenly colored with dirty violescent indigo. When the solution was treated with ammonia after the previous removal of the precipitate. which was produced with an insufficient amount of ammonia and showed the color reaction, the precipitate thus formed remained almost colorless with iodine.

(5) As already mentioned above, the basic acetate precipitate which was formed from a solution containing lanthanum acetate and a considerable quantity of yttrium acetate, did not show the color reaction with iodine. But when the method of fractional precipitation with ammonia

was applied to such a solution, the precipitate in earlier stages did not show the color reaction, while that in later stages took on an indigo color with iodine. This showed that the precipitation of basic yttrium acetate occurred before that of basic lanthanum acetate.

The above-mentioned experimental results seem to support our interpretation on the mechanism of the effect of some anions and cations. Hitherto little attention was paid by earlier authors to the quantity of ammonia used, but it is obvious from the above-mentioned experiments that the amount of ammonia added to form basic acetate precipitate plays always an important role.

Summary. (1) The color reaction between iodine and basic acetate is not, as is often believed, peculiar to lanthanum. It is shown also by praseodymium, neodymium and samarium.

(2) The absorption maximum of iodine-basic acetate shifts to shorter wave-length side with the decrease of the basicity of the rare earth elements.

(3) The color change of iodine-basic acetate with the lapse of time was studied photometrically.

(4) It was confirmed that the sorption isotherm holds good in the cases of the basic acetates of lanthanum, praseodymium and neodymium.

(5) The effect of other ions on the color reaction was discussed.

A part of the cost of this study was defrayed from the grant of the Ministry of Education, for which the authors wish to record their thanks.

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Mechanism of Oxidation of Methanol Vapour by the Use of Heavy Oxygen.

By Noriyoshi MORITA.

(Received May 18, 1946.)

Vapour of methanol was burned in heavy oxygen, and the heavy oxygen contents of the products, water and carbon dioxide, were determined. Thus it was examined with which atom, hydrogen or carbon, the oxygen atom, previously existing in methanol composition, will remain combined preferencially. The results show that the difference in heavy oxygen contents is small, and it is concluded that during the oxidation the oxygen in methanol goes through some condition where it equalizes with supplied oxygen, such as intermediate production of peroxide-like substance. The effects of the addition of tetraethyl lead and of the presence of catalyser were also examined, and it was observed that they somewhat promote the separation of carbon-oxygen bond rather than hydrogen-oxygen bond in methanol.

Introduction. When the combustion reaction of methanol vapour goes on stepwisely in the following way:

$$CH_3OH + \frac{1}{2}O_2^* = HCHO + H_2O^*,$$

$$HCHO + \frac{1}{2}O_2^* = HCOO^*H,$$

$$HCOO^*H + \frac{1}{2}O_2^* = COO^* + H_2O^*,$$

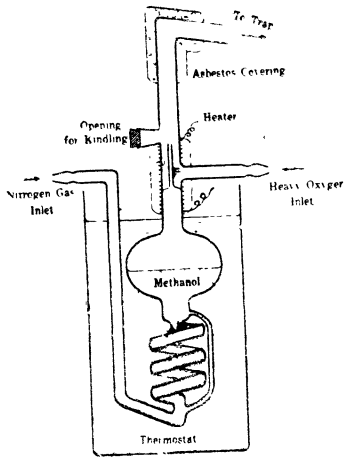
(O* indicates supplied oxygen marked with heavy oxygen),

then after the reaction, the methanol oxygen, previously contained in its composition, will come to exist combined with carbon. And therefore if we assume that the excess density of supplied heavy oxygen be a (determined as water), the excess density of oxygen of produced water and of carbon dioxide must be a and $\frac{1}{2}a$, respectively. In moderate reactions some evidences as to the firmness of carbon-oxygen bond have been disclosed. For example, when alcohol esterifies with organic acid, dissociation of alcohol occurs at O-H bond, not at C-O bond.[1] However, when we consider the steric constitution of methanol molecule, we find, on one hand, that the bond energy of C-O is only 70.0 kcal/mol compared with 110.2 kcal/mol of O-H bond and, on the other, that the atomic distance of C-O, 1.43A, is much larger than that of C-H, 1.09A, and accordingly

(1) B. Holmberg, *Ber.*, **45** (1912), 2997; E. H. Ingold and C. K. Ingold, *J. Chem. Soc.*, **112** (1932), 756; M. Polanyi, A. L. Szabo, *Trans. Faraday Soc.*, **30** (1934), 508.

the -OH group of methanol molecule must stand out of $-CH_3$ group. From this point of view, it is probable that the methanol molecule be separated at C-O bond and yield free methyl radical as the foremost stage of reaction, especially in such severe one as combustion. In this case the relation of excess densities between produced water and carbon dioxide (measured as converted water) is the reverse of the first case, and must be larger in carbon dioxide. Moreover, as the third case, we can consider some stage of reaction during the whole oxidation, where both oxygens, i.e. one in methanol composition and the other supplied for combustion, are equalized, such as intermediate production of peroxide CH_3OO^*H. When this is the case the resultant compositions of oxygens, combined with carbon and hydrogen atoms, will be nearly equal with each other. The main aim of the following experiments is to determine which is the case, and in addition to confirm the existence or the nonexistence of the effects due to the added impurities or catalysers.

Experimental procedures.



The apparatus used for combustion of methanol vapour in heavy oxygen is shown in the accompanying figure, all of which is made of Pyrex glass. Liquid methanol is to be placed in vapour saturation vessel[2] heated to desired temperature by thermostat. Through this, introducing nitrogen gas with controlled velocity, saturated vapour of methanol with known velocity is obtained and let it gush out from a narrow jet 1 mm. in diameter, into a concentric tube about 10 mm. in diameter through which heavy oxygen with known velocity is passed. This part of the apparatus is heated up to about 100°C. to avoid the condensation of methanol vapour. After kindling flame, the gas and vapour mixture of combustion is introduced into an ice-cooled trap and then into a liquid-air-cooled trap (both not shown in the figure). The carbon dioxide, solidified in the second trap, is reduced to water by hydrogen with known isotopic composition, by the use of Ti-ThO_2 catalyser. Lastly, both of the waters, i.e. one condensed in the first trap and the other obtained by the reduction of carbon dioxide, are purified and their excess densities are measured. If we wish to carry on the oxidation in the existence of catalyser, the methanol vapour saturated in nitrogen gas should be mixed beforehand with heavy oxygen and then introduced over the catalyser heated to the desired temperature.

(2) N. Morita, T. Titani, this Bulletin, **12** (1937), 358, N. Morita, *J. Chem. Soc. Japan*, **62** (1941), 65.

The purifications of the resultant waters for density measurements are done by the ordinary method described in other places.[3] When the oxygen content of reacting mixture is not sufficient to complete the oxidation, a large quantity of impurities will be included in the produced water. Then it is mixed with potassium carbonate, dried at about 200°C. in vacuum beforehand, in the proportion of 5 gr. of it to about 10 gr. of water, and heated gently in water bath to boil out these impurities (mainly methanol and aldehyde). After the smell of methanol vapour has nearly completely vanished, the water is distilled in vacuum, and then purified with the ordinary process. During this process the loss of water is so little that we can neglect changes in isotopic composition of the water, and moreover the exchange reaction of oxygen atoms between water and carbonate is also negligible under these conditions.[4]

Results. For the purpose of confirming the excess densities of hydrogen in methanol composition, of hydrogen gas in bomb to be used for the reduction of carbon dioxide and of heavy oxygen gas, methanol vapour and hydrogen gas in bomb are burned in the air and the latter in heavy oxygen. Table 1 shows the excess densities of the resultant water compared with ordinary water.

Table 1. Excess densities of resultant waters in γ.

Reaction	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Mean
Methanol + Air	5.9	7.0	8.5	5.8	+6.8
Hydrogen in bomb + Air	3.0	3.0	1.4	—	+2.5
Hydrogen in bomb + Air	58.7	60.1	—	—	+59.4

Considering the excess desnsity of 7.0 γ of oxygen in the air compared with that of ordinary water,[5] we can get the results shown in Table 2.

Table 2. Excess densities in γ, determined as water.

Hydrogen of methanol	=	+ 6.8	−7.0	= − 0.2 γ
Hydrogen gas in bomb	=	+ 2.5	−7.0	= − 4.5 γ
Heavy oxygen gas	=	+59.4	+4.5	= +63.9 γ

By the use of those reagents the combustion experiments of methanol vapour are made and we obtained the results shown in Table 3.

The results obtained by the addition of about 5% tetraethyl lead to liquid methanol in the vapour saturation vessel and by the use of copper catalyser heated to 300°C. are shown in Table 4.

(3) For example: N. Morita, *J. Chem. Soc, Japan*, **58** (1937), 1151; T. Titani, N. Morita, this Bulletin, **13** (1938), 409.

(4) T. Titani, N. Morita, K. Goto, this Bulletin, **13** (1938), 329; T. Titani, K. Goto, ibid., **14** (1939), 77.

(5) N. Morita, *J. Chem. Soc. Japan*, **57** (1936), 176; N. Morita, T. Titani, this Bulletin, **11** (1936), 414.

Table 3. Combustion of methanol vapour in heavy oxygen.

Subject	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
Temperature of Thermostat in °C	50.0	50.0	50.0	50.0	56.0
Flow velocity of Nitrogen Gas in cc/sec	0.55	0.55	0.73	0.70	0.30
Flow velocity of Methanol Vapour in cc/sec	0.63	0.63	0.84	0.80	0.70
Flow velocity of Heavy Oxygen Gas in cc/sec	1.45	2.02	1.80	1.66	1.40
Excess Densities of, in γ: Water, obtained by Combustion	45.7	45.0	45.1	44.9	46.5
Excess Densities of, in γ: Water, reduced from Carbon Dioxide	—	—	48.7	43.3	44.7
Excess Densities of, in γ: Oxygen, combined with Hydrogen Atom	45.9	45.2	45.3	45.1	46.7
Excess Densities of, in γ: Oxygen, combined with Carbon Atom	—	—	53.2	47.8	49.0

Table 4. The effect of the addition of tetraethyl lead and of the existence of copper catalyser.

Subject	Addition of tetraethyl lead	Existence of copper catalyser: Exp. 1	Exp. 2
Temperature of Thermostat in °C	55.0	50.0	50.0
Flow velocity of Nitrogen Gas in cc/sec	0.32	0.47	—
Flow velocity of Methanol Vapour in cc/sec	0.64	0.54	—
Flow velocity of Heavy Oxgen Gas in cc/sec	1.60	0.56	
Excess Densities of, in γ: Water, obtained by Combustion	44.4	40.7	39.1
Excess Densities of, in γ: Water, reduced from Carbon Dioxide	48.4	—	41.9
Excess Densities of, in γ: Oxygen, combined with Hydrogen Atom	44.6	40.9	39.3
Excess Densities of, in γ: Oxygen, combined with Carbon Atom	52.9	—	46.4

Discussion.

As shown in Table 2 the excess density of the heavy oxygen used for combustion is 63.9 γ, so that if we consider the case where both of the oxygens, i.e. one originally contained in methanol composition and the other in the supplied gas for combustion, are completely mixed by some intermediate reaction, and assuming the former is the same in its isotopic composition as the oxygen of ordinary water, then it is clear from the reaction equation:

$$CH_3OH + \frac{3}{2}O_2 = CO_2 + 2H_2O,$$

the excess densities of either of the oxygens, combined with hydrogen or carbon atom, must be $63.9 \times 3/4 = 48.9$ γ, both determined as water. On the contrary, when the oxygen in methanol composition remains fixed with either carbon atom or hydrogen atom throughout the combustion reaction, then after the reaction the excess density of that oxygen must become $63.9 \times 1/2 = 32.0$ γ and that of the other remains unaffected, that is 63.9 γ. It is shown by Table 3 that in variant proportions and velocities of mixed gases the resultant water and carbon dioxide have nearly the same composition of isotope. This result coincides with the first case, where the oxygen in methanol composition goes through some stage throughout the combustion reaction to equalize its state with that of supplied oxygen,

and seems to exclude the second case, where the possibilities of dissociation of methanol molecule may be considerable at the first stage of the combustion, such as to form aldehyde and hydrogen or methyl and hydroxyl radicals. Surely it is possible that the exchange reaction between water and carbon dioxide would occur after the production. But judging from the experimental procedures it is clear that the exchange reaction in the liquid phase must be negligible, and that in the homogeneous phase it is possible only in the very high temperature such as in the flame part of the reaction system, where the extreme dissociations of methanol and oxygen molecule to atoms or ions may occur. The possibility of this case, however, is itself included in the statement that the oxygen in methanol goes through some stage to equalize its state with that of the supplied oxygen. Nevertheless, from the point of activation energy for reaction, it is more pertinent to consider the production of peroxide such as CH_3OOH or $CH_2(OH)_2$ in the early stage of combustion, as it advanced as the intermediate stage of hydrocarbon oxidation, than to postulate the dissociation to atoms or ions.

By the more detailed examination of Table 2, it is shown that the oxygen combined with hydrogen is always somewhat lighter than that combined with carbon. From this, it seems as if the oxygen atom of methanol were more tightly bound with hydrogen atom than with carbon, or in other words, at the combustion reaction the C-O bond of methanol is a little more easily dissociated than O-H bond. The differences shown in the experimental results are small, and then, considering the difficulty of the experimental procedures, it may be possible to attribute this difference to some systematic error such as caused from the difference in the purification processes of both kinds of water. However, it may also be possible to consider the dissociation of some members of methanol molecules to produce free methyl radicals or such others at the early stage of the combustion reaction. The acceptance of this postulate is more convenient to elucidate the results shown in Table 4. There is no conspicuous difference in the results shown in this Table compared with Table 3. But the addition of tetraethyl lead or the existence of copper catalyser seems somewhat to increase the difference in the isotopic compositions between the oxygen combined with hydrogen and that with carbon. In other words, the addition of tetraethyl lead or catalyser may promote the production of free radical in the oxidation reaction of methanol vapour, which is very probable from the catalytic power of these addition substances. But for concluding this hypothesis the experimental repetition is not sufficient and some more elaborate experiments are necessary.

In conclusion, the writer wishes to express his hearty thanks to Prof. K. Onda, of this University, for the loan of the methanol and tetraethyl lead, and to Yahagi Kogyo & Co. for kindly giving him liquid air used in this investigation. The writer is also indebted to Nippon Gakujutsu

Shinkokai (Society for Promotion of Scientific Investigations, Japan) for the financial assistance.

Faculty of Engineering, Nagoya University.

Studies on Foams. (I). The Foaminess and Foam Stability of Liquid Mixtures.

By Masayuki NAKAGAKI.

(Received April 17, 1948.)

Introduction. It is often said that the foaminess and the foam stability of liquid are not always parallel with each other. For example, an aqueous solution of saponin produces a more stable but less voluminous foam than that of n-butyl alcohol, when they are shaken under the same condition. It is known, however, that saponin solution readily forms solid skin on their surface, so the structure of foam of the solution may differ entirely from those of alcohol solution. Under these circumstances, it may be more reasonable to compare solutions of common constituents but varying compositions than to compare solutions of different constituents, in order to see whether foaminess and foam stability are parallel or not. By such reason, mixtures of the liquids of low molecular weights were tested, because they make no skins on their surfaces.

The Foam Formation of the Ternary System, Ethyl Alcohol-Glycerol-Water. Foam formation has been tested with a test tube of 18.5 c.c. capacity containing 10 c.c. of solution by shaking up and down with hand for 30 min. at the rate of 3 times per sec. in the amplitude of 25 cm. The following three quantities have been measured: the height of foam zone immediately after the end of shaking, (A_0), which measures foaminess; the time required for a part of liquid surface to appear as a result of collapse of foam zone, (t), that is the duration of foam zone; the time required for whole bubbles to disappear after the appearance of a part of liquid surface, (Δt). The value of Δt is the time expended to disappear by the bubbles arrang d in one sheet all over the cross section of the test tube of diameter 1.5 cm., so that this is a measure of the strength of the liquid lamina constituting the upper surface of each bubble.

Relations between the composition of the ternary system expressed by weight per cent and the quantities of A_0, t, and Δt are shown in Fig. 1, 2, and 3, respectively. In these figures, W, E, and G represent water, ethyl alcohol. and glycerol respectively; PQ are 45 per cent line of ethyl alcohol. In Figs. 1 and 2, two maxima A and B, the latter including B′ which is regarded as the extension of B, are observed, and A_0 and t become nearly zero when the composition of glycerol is increased. On the contrary, in Fig. 3, maximum C is observed in the range of high concentration of glycerol, besides two maxima A and B described above. The new maximum C is extended toward W and covers the maximum B′.

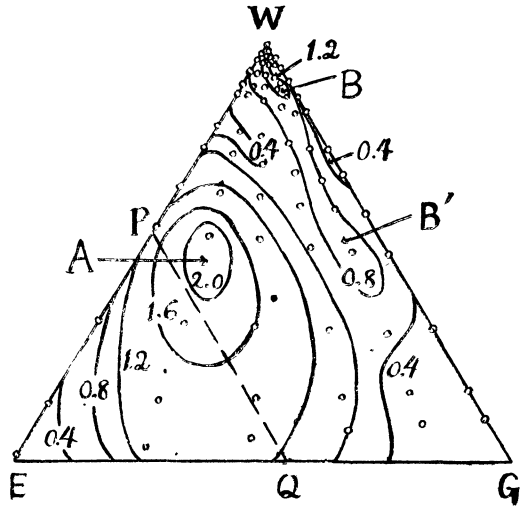


Fig. 1. A_0 (cm.).

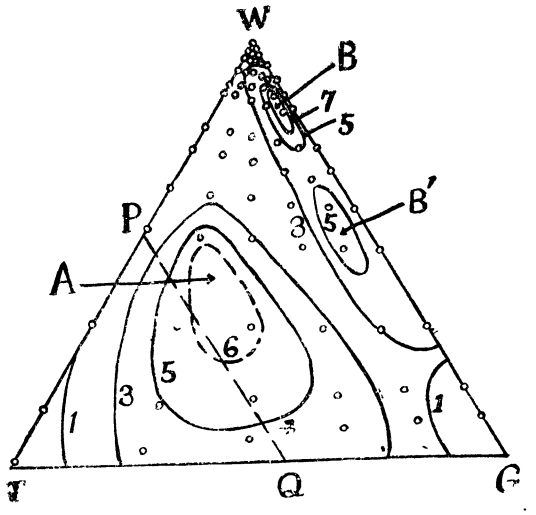


Fig. 2. t (sec.).

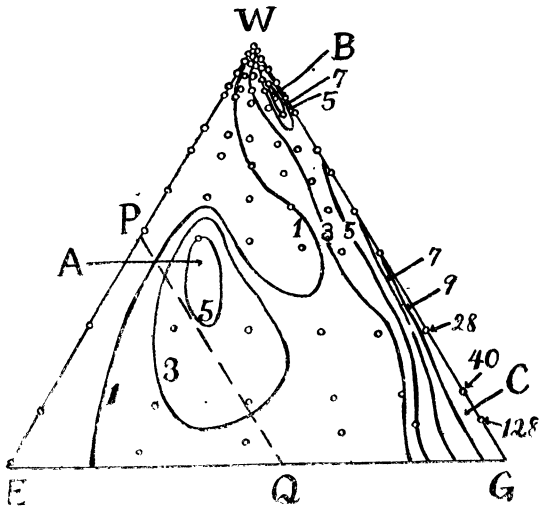


Fig. 3. Δt (sec.).

Foaminess and Foam Stability. Three quantities A_0, t and Δt, are not independent but related one another as follows:—

Bubble stability Δt is thought to be proportional to the duration of a single bubble, which is directly subject to the strength of liquid lamina constructing the upper part of a bubble.

Duration of foam zone t is thought to be subject to both the duration of each bubble (Δt) and the amount of bubbles in the foam, the latter being proportional to the foam zone height (A_0). Among these, A_0 is more predominant to t, since Fig. 2 is entirely parallel to Fig. 1 but not to Fig. 3.

At last, foam zone height A_0 is considered to be the superposition of two actions; the one is to form bubbles by the mixing of gas with liquid, and the other is to make bubbles escape from liquid. If, then, the rate of formation of bubbles by the admixture of gas and liquid is nearly constant under the same conditions of shaking, the foam zone height A_0 should be proportional to bubble stability Δt. Actually, this circumstance is realized near the maximum A and B as is shown in Figs. 1 and 3. As an exception, A_0 and Δt are not parallel in the neighbourhood of G, where the viscosity of the system is larger than ten times of that of water. As easily seen, the duration of bubble once formed, Δt, is largely increased, when the viscosity of liquid is increased, owing to the diminution of the velocity of flow in a liquid lamina. This idea[1] is stated early by J.W. Gibbs, which is referred to recently by S. Ross,[2] G. D. Miles, Leo Shedlovsky and J. Ross.[3] On the one hand,

(1) S. Berkman and G. Egloff, "Emulsions and Foams," p. 141, New York (1941).
(2) S. Ross, *J. Phys. Chem.*, 47, 266 (1943).
(3) G.D. Miles, Leo Shedlovsky and J. Ross, *J. Phys. Chem.*, 49, 93 (1945).

however, the mixing of gas with liquid is considerably obstructed by the high viscosity, and foam zone height A_0 becomes nearly zero, as supposed by E. G. King.[4]

The Foam Formation of Sulphuric Acid Solutions. Another example that the foaminess and foam stability are not parallel owing to the high viscosity of system is shown in Table 1, with respect to the aqueous solutions of sulphuric acid. Viscosity values taken from the "International Critical Tables" are also cited in the last column. Zero of foaminess or foam duratien means that the shaking does not produce enough bubbles to cover all over the surface, and bubble stability corresponding to them shows the time required for the bubbles to disappear. From this table, the decrease of foaminess and foam duration and the increase of bubble stability are distinctly recognized when the viscosity of system becomes more than eight times as large as that of water.

Table 1. Sulphuric Acid.

Concentration Weight per cent	Foaminess A_0 (cm.)	Foam Duration t (sec.)	Bubble Stability Δt (sec.)	Relative Viscosity (η/η_W)
91.1	0.0	0.0	28	26.3
79.4	0.0	0.0	11.7	22.0
62.3	0.0	0.0	5.3	7.7
41.4	0.4	2.0	0	3.2
21.8	0.4	2.0	0	1.8
0.0	0.4	1.9	0	1.0

Physico-Chemical Properties of the Ternary System. Some physico-chemical properties of the ternary system, ethyl alcohol-glycerol-water are measured, to interpret maxima A, B and C in the diagrams of foam formation of the system. Viscosity, measured by Ostwald's viscometer at 30°C, surface tension by Traube's staragmometer at room temperature 17°C, and density by Ostwald's pycnometer at 30°C, are shown in Figs. 4, 5 and 6, respectively. These are shown, referring to those of water as unity. The volume contraction on admixture calculated from the density data is also shown in Fig. 7 in c. c. per 100 g. of solution.

The Interpretation of Maxima in Foam Formation. The maximum B in Figs. 1, 2 and 3 found in the region of low concentration of ethyl alcohol is thought, as is often said, to be due to the surface activity of ethyl alcohol, referring to Fig. 5, where steep diminution of surface tension of the system is recorded in this region. The maximum C in Fig. 3 is supposed, as already pointed out, to be due to the high viscosity

(4) E.G. King, *J. Phys. Chem.*, 48, 141 (1944).

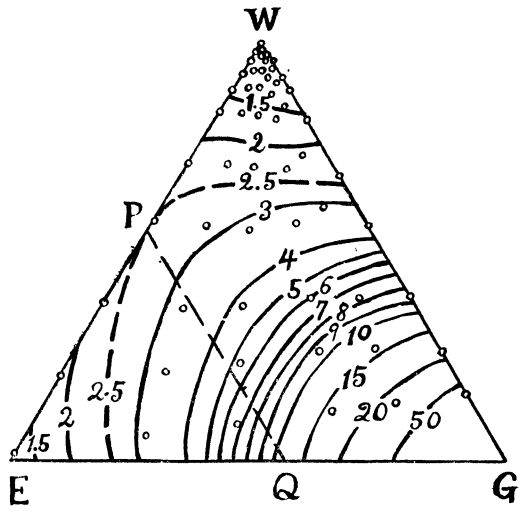


Fig. 4. η/η_w.

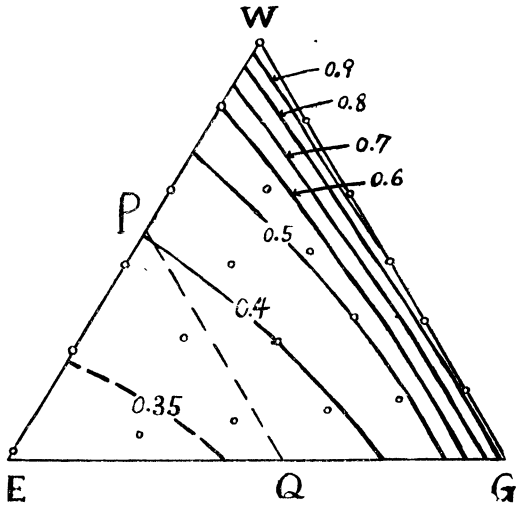


Fig. 5. γ/γ_w.

of the system. Comparing Fig. 3 with Fig. 4, it is noticed that the maximum C is abnormally biassed to the portion of the low concentration of ethyl alcohol, which is not found in the viscosity-composition diagram. This effect is already recognized by O. Bartsch,[5] and the interpretation is that the surface active alcohol drives out the surface inactive glycerol from the wall of foam.

Then how the maximum A in Figs. 1, 2 and 3 is interpreted? Referring to the data cited before, it is found that the density and the surface tension have no relation to this maximum A in foam formation.

(5) O. Bartsch, *Kolloid-Beihefte.*, 20, 1 (1925).

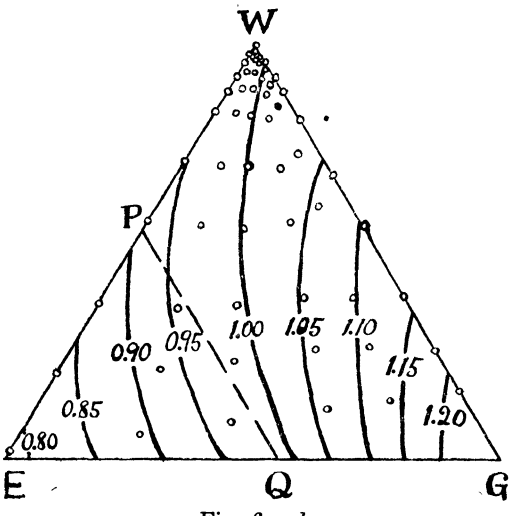


Fig. 6. *d*.

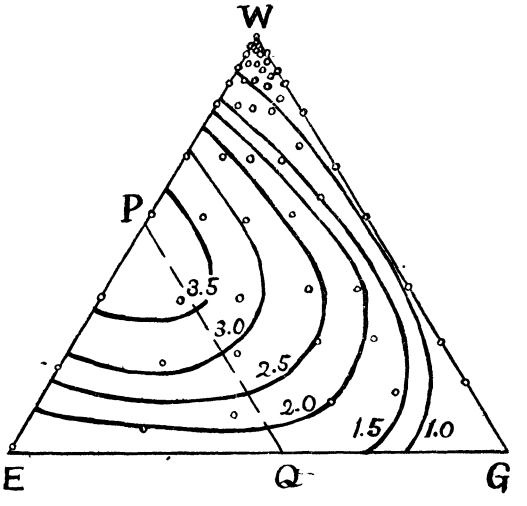


Fig. 7. ΔV (c c./100 g.)

This maximum may be interpreted, by the assumption that the volume contraction on admixture is in close connection with foam formation and viscosity has an auxiliary influence to it; that is to say, the general feature of the maximum A is parallel to the volume contraction ΔV in Fig. 7, and the slope of the maximum A on the side of P is influenced by the viscosity change of the system. Volume contraction might suggest a certain structure formation in the solution that is in favour of foaming. Such an idea, however, should be examined by further examples.

Summary. The height of the foam zone, the duration and the

stability of foam of the ternary system, ethyl alcohol-glycerol-water have been measured. As the result three maximum points A, B and C in the diagrams of these properties are found. The maximum B in the region of low concentration of ethyl alcohol is due to the decrease of surface tension. The maximum C, which is found in the bubble stability diagram while absent in foaminess and foam duration diagrams, may be ascribed to the high viscosity of the system. The same effect is found also in the case of the aqueous solution of sulphuric acid. The maximum A is supposed to be parallel to volume contraction on admixture.

The author wishes to express his hearty thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement.

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A Modified Derivation of BET Isotherm in Statistical Mechanics*.

By Yutaka MIYAHARA.

(Received June 2, 1948.)

1. S. Brunauer, P. H. Emmett and E. Teller[1] have generalized the Langmuir's adsorption theory to multimolecular adsorption and obtained an adsorption isotherm (BET isotherm). This adsorption isotherm gives a fair agreement with experimental data, and is now widely utilized in obtaining informations on the surface area of adsorbent. The original derivation of the isotherm has been done on the basis of kinetic theory; while several authors[2] have studied this problem from the point of view of statistical mechanics. In this paper, the author will derive the same isotherm by the saddle point method of statistical mechanics, free from erroneous calculation of permutations and combinations. The model of the present theory is almost the same as the other authors.

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* Read at the lst Annual Meeting of the Chemical Society of Japan held at Tokyo on April 3, 1948.

(1) S. Brunauer, P. H. Emmett, and E. Teller. *J. Am. Chem. Soc.* **60** (1938), 3309.

(2) T. L. Hill; *J. Chem. Phys.* **14** (1946), 263.
M. Dole; *J. Chem Phys.* **16** (1948), 25.

2. The model, on which the theory is based, is analogous to the one in Hill's paper[2]; on the flat surface of adsorbent there are S sites for adsorption, S_0, S_1, S_2, ... S_j, ... which are covered, respectively, by 0, 1, 2, 3, ... j, ... layers of adsorbed molecules. In equilibrium, the ratio of these S_js will become a constant value. For the sake of simplicity, the possible positions of adsorbed molecules in multilayers are assumed to be in a vertical line from any sites, as shown in Fig. 1.

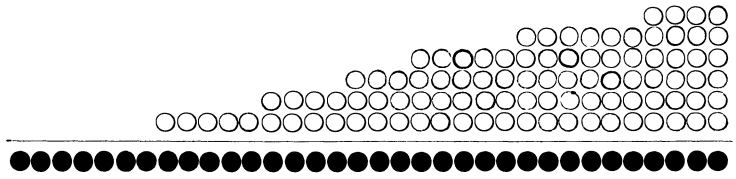

Fig. 1.

Now there are $S_1 + S_2 + S_3 + \cdots\cdots$ adsorbed molecules in the first layer, and therefore, the partition function for this layer is given by $f_1^{s_1+s_2+s_3+\cdots}$, where f_1 denotes the internal partition function of a molecule in the first layer. In the same manner, the partition function for the second layer is given by

$$f_2^{s_2+s_3+s_4+\cdots}$$

and so on.

It is assumed, as has been done in the BET theory, that the partition function of the j-th cell ($j>1$) is identical with each other, and they are denoted by f. The complete partition function for the adsorbed system is, then

$$\theta = \sum \frac{S!}{\prod_0^\infty S_j!} f_1^{s_1+s_2+s_3+\cdots} f^{s_2+s_3+\cdots} f^{s_3+s_4+\cdots}$$

with the conditions $\sum_0^\infty S_j = S$, $\sum_0^\infty jS_j = N$; N means the total number of adsorbed molecules. θ may be rewritten as follows;

$$\theta = \sum \frac{S!}{\prod_0^\infty S_j!} f_1^{s_1} (f_1 f)^{s_2} (f_1 f^2)^{s_3} \ldots (f_1 f^{j-1})^{s_j} \ldots$$

Putting $k_0 = 1$, $k_1 = f_1$, $k_2 = f_1 f$, ... $k_j = f_1 f^{j-1} (j \geq 1)$..... (1)

then

$$\theta = \sum S! \prod_0^\infty \frac{k_j^{s_j}}{S_j!}$$

For calculating θ, then modular function ϕ is defined as

$$\phi = (\sum_0^\infty x^j k_j)^s$$

It is evident that θ is the coefficient of x^N in the expanded series of ϕ in x. According to the Cauchy's theorem,

$$\theta = \frac{1}{2\pi i}\oint \frac{(\sum x^j k_j)^s}{x^{N+1}}dx = \frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} e^{s\log(\sum x^j k_j)-(N+1)\log x}dx$$

θ may be calculated approximately by the saddle point method. If the saddle point in integland is denoted by α, then it follows that

$$\log\theta \fallingdotseq S\log(\sum \alpha^j k_j) - N\log\alpha$$

where α can be determined by

$$\frac{d}{dx}\left\{S\log(\sum x^j k_j) - (N+1)\log x\right\} = 0$$

or

$$\frac{N}{S} = \frac{\sum_0^\infty j\alpha^j k_j}{\sum_0^\infty \alpha^j k_j} \qquad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

For the free energy F of the adsorbed system, it holds

$$-\frac{F}{kT} = \log\theta = S\log(\sum \alpha^j k_j) - N\log\alpha$$

For the partial potential μ of the molecules

$$\frac{\mu}{kT} = \frac{1}{kT}\frac{\partial F}{\partial N} = \log\alpha$$

For the abosolute activity of molecules is, then given by

$$\lambda = e^{\mu/kT} = \alpha$$

In the gaseous phase the absolute activily λ' is, as shown[3], given by

$$\lambda' = \frac{p}{kT}\frac{h^3}{(2\pi mkT)^{3/2} j(T)}$$

In equilibrium, λ is equal to λ'; therefore,

$$\alpha = \frac{p}{kT}\frac{h^3}{(2\pi mkT)^{3/2} j(T)}$$

Substituting this value of α into equation (2), the adsorption isotherm are obtained in the form,

$$\frac{N}{S} = \frac{\sum j\alpha^j k_j}{\sum \alpha^j k_j}$$

(3) R. H. Fowler and E. A. Guggenheim; "Statistical Thermodynamics", (1939).

From (1), it follows that

$$\frac{N}{S} = \frac{af_1}{(1-af)(1-af+af_1)}$$

or, in accordance with the BET's representation,

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)}$$

where v is the total volume of adsorbed vapour, v_m the volume for the monolayer adsorption, respectively.

The constants c, x are respectively given by $c = \frac{f_1}{f}$ and $x = af$..

If it is assumed that the higher layers of adsorbed molecules other than the first are in liquid of soled state, then f can be represented by saturation pressure p_s, that is,

$$\frac{1}{f} = \frac{p_s}{kT} \frac{h^3}{(2\pi mkT)^{3/2} j(T)}$$

then

$$x = \frac{p}{p_s}$$

The constant c can be written in the following form,

$$c = \frac{f_1}{f} = Ke^{(E_1-E_L)/RT}$$

where E_1 and E_L are, respectively, the heat of adsorption to naked surface and the heat of vapourisation or sublimation.

Summary. (1) The BET adsorption isotherm was derived by statistical mechanics, using the saddle point method.

(2) The constants in BET isotherm can be represented by the internal partition functions of the adsorbed phase.

The author is indebted to Professor Dr. I. Sano, Dr. K. Suzuki and Dr. T. Sakaki for helpful comments.

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The Extraction of Germanium and Gallium from Germanite.

By Kazuo SAITO.

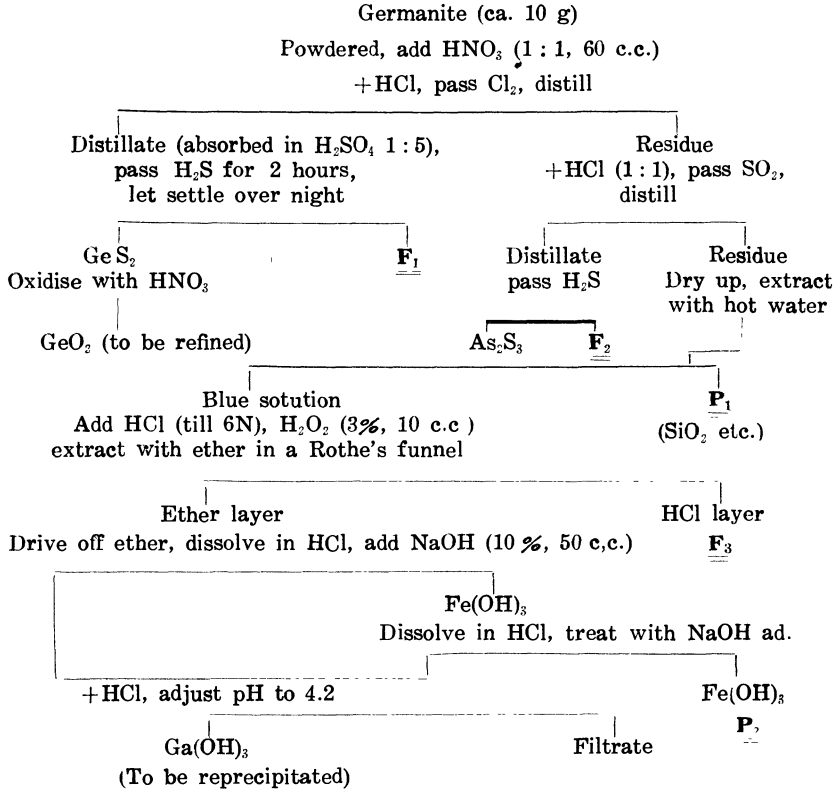
(Received June 1, 1948.)

The author has planned to prepare pure germanium compound, which is available as the standard substance in the studies of the chemistry of germanium, from germanite in small scale. The main constituents of the mineral is as follows:[1]

Cu	45.60%
Fe	7.22
Ge	6.20
Zn	2.61
Pb	0.19
S	31.34
As	5.03
SiO_2	0.75
Total	98.94

The minor elements are Ga, Na, P, Mg, Ca, Ti, Al, Mo, W, Sb, Mn, V, Au, and (Hg); they are detected by spectroscopic method with E-2 spectroscope (Adam Hilger).

Table 1.



(1) The quantitative analysis was carried out at Tsumeb, Africa.

The course of separation is systematised in Table 1.[2] Germanium is distilled from hydrochloric acid solution in the current of chrorine; the yield is about 6.1?.

Preparation of pure germanium dioxide. The spectroscopic test of the unrefined germanium dioxide indicates that the main impurities are Si, Fe, Mg, Na, Ca and Ti. They are all common elements and those elements which would be caused by imperfectness of the separation are not found. So it is unnecessary to be too timid of incompleteness of the separation in such a small scaled work in laboratory.[3]

Several methods[4] to remove the minor elements had been tried and in consequence it could be understood that too much complicated operations are not desirable for the preparation of a pure compound in this case. Thus the following process is recommended. Germanium dioxide is dissolved in caustic soda solution. To oxidise arsenic that would be accompanied, pass chlorine gas though the alkaline solution; add hydrochloric acid and distill. The distillate is absorded in distilled hydrochloric acid. Germanium hydroxide produced by the hydrolysis in the flask adheres so tightly to the bottom of the vessel, that the supernatant liquid can be decanted without any loss of the precipitate. Add cold water into the vessel, shake well and decant it out; repeat this washing for several times. (If the distillate be absorbed in water, the yield of the pure hydroxide will be better, but the precipitate does not adhere to the bottom so tightly, therefore various operations are required for its separation.) Dry the vessel at room temperature (applicatton of heat causes contamination of silicon from the glass), scrape off the precipitate and ignite it in a platinum crucible.

Germanium dioxide thus obtained is snow white. The spectroscopic examination of it does not indicate any contamination. (However, as germanium oxide is relatively volatile in the arc, the temperature should be kept comparatively low; therefore it is afraid that the line of several elements might not appear.)[5] The apparent atomic weight of germanium in this oxide is found between 72 and 73, and it can be applied as the standard substance.

Extraction of gallium and its examination. For the extraction of gallium, Rothe's extraction by ether was carried out.[6] As arsenic is

(2) R. Berg & W. Keil; *Z. anorg, allg Chem.* **209** (1932) 383.
L. Dede & W. Russ; *Ber.* **61** (1928) 2451.
(3) H. J. Abrahams & J.H. Millers; *J. Am. C em. Soc.* **54** (1932) 86.
(4) E.B. Johnson & L.M. Dennis; *J. Am. Chem. Soc.* **47** (1925) 790.
W. Keil; *Z. anorg. allog. Chem*: **152** (1926) 101,
(5) J. Papish; *J. Am. Chem. Soc.* **49** (1927) 3028.
(6) R. Berg & W. Keil; 1. c.
W. F. Hillebrand & G.E.F. Lundell, "Applied Inorganic Analysis", p. 106.

also extracted with ether from hydrochloric acid solution, the removal of it is required. For this purpose the distillation of arsenic trichloride in the current of sulphur dioxide is recommended. In order to extract gallium completely from the acidic solution with ether, it is desirable to extract it together with large amount of trivalent iron, which can be removed afterwards simply. After the separation of iron, add hydrochloric acid and adjust the pH to 4.2 with aqueous ammonia using methyl red as indicator. Excess of alkali should be avoided. The yield of gallium is about 0.63% of the ore.[7]

In order to examine the accuracy of the extraction, the author has tried to test each fraction, where the loss of gallium would be found, with spectroscopic method (underlined fractions of Table 1). Aluminium alum, in which the absence of gallium has been confirmed, is applied as the carrier. To F_1, F_2 and F_3 or the Table 1 add 20 cc of 1% alum solution and precipitate hydrated oxide of aluminium as usual.

The arc-spectra were observed with E-2 spectroscope, with the aid of carbon electrode. The conditions were as fellows:

Voltage: 100V D.C. Current: 4-5A Exposure: 2 minutes
Slit: 0.01 mm Plate: Fuji Process $4'' \times 10''$.

The lines found on the plate are as follows:

Table 2.

	F_1	F_2	F_3	P_1	P_2
2500.2 Å	—	—	+	—	—
2944.2	—	—	+	—	—
2943.6	—	—	++	—	+

The appearance of these lines indicates that on the carbon electrode only little gallium is present[8] (F_3, 0.00n mg Ga, P_2, 0.00 on mg Ga). Taking the amounts of the precipitates into consideration, the gallium contents of these fractions must be below one milligram. Thus the above method is recommended for the extration of gallium from germanite. The gallium oxide thus obtained is very pure.

Summary. The author has succeeded to extract germanium and gallium of satisfactory quality almost quantitatively in small scale. Germanium oxide can be refined by redistillation and hydrolysis, and the product is applicable as the standard substance for the chemical study. It is confirmed that Rothe's extraction is a suitable method for

(7) The gallium content of germanite is reported to correspond 0.71, 0.57 and 0.74% (Gmerins Handbuch).

(8) J. Papish & A. Holt; *J. Phys. Chem.* **32** (1928) 142.

the preparation of gallium from germanite.

The author wishes to express his sincere gratitude to Prof. Dr. Kenjiro Kimura for his kind guidance and encouragement, and to Mr. Yohachiro Okamoto and Mr. Kinïchi Sakurai for their kind supply of the mineral; the author also desires to thank Miss Hatsumi Tamagawa for her assistance in the experimental work.

The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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The Seperation and Purification of Rare Earth Elements from Monazite (I)

By Hisaichi ARAKAWA

(Received December 13, 1945.)

The separation of rare earth elements is particularly difficult on the large scale in the industrial process, and the usual commercial method of separating these elements in their mixture obtained from monazite ores requires large quantities of oxalic acid, ammonium oxalate and special reagents, which are difficult to obtain in this country. Therefore the author investigated a new method that does not require oxalates and other special reagents.

1. Materials. The new materials used in this investigation were monazite from Sengan, in Korea. The composition of two samples are shown in Table 1.

Table 1.

No.	$ThO_2 + R_2O_3$	ThO_2	P_2O_5	MgO	CaO	Al_2O_3	Fe_2O_3	SiO_2	Ignition loss	H_2O	total
	%	%	%	%	%	%	%	%	%	%	%
1.	64.03	6.70	23 61	0.74	0.57	1.38	7.48	3.00	—	—	100.81
2.	61.44	6.52	13.80	0.08	4.95	19.50		2.10	0.56	0.32	102.7

2. Extraction of thorium and rare earths from monazite: For the decomposition of monazite, there are several methods, such as the

sulphuric acid method, the carbon method, or the method by alkali-fusion.

The author, at first, studied the sulphuric acid method.

Powdered monazite in concentrated sulphuric acid is heated to render thorium and rare earth soluble in water. After cooling, it is slowly mixed with cold water and allowed to stand overnight. It is then filtered. The filtrate contains thorium and rare earths, iron, aluminium, phosphoric acid, etc. The representative methods in which thorium and rare earths are separated from one another and from other elements in the extracted solution are as follows:

(a) The fractional precipitation of thorium phosphate, as a white isinglasslike precipitate, produced upon addition of ammonia water or magnesia to the extracted solution.

(b) The removal of the cerium group rare earths double compound of alkali sulphate, produced by addition of the reagent to the extracted solution.

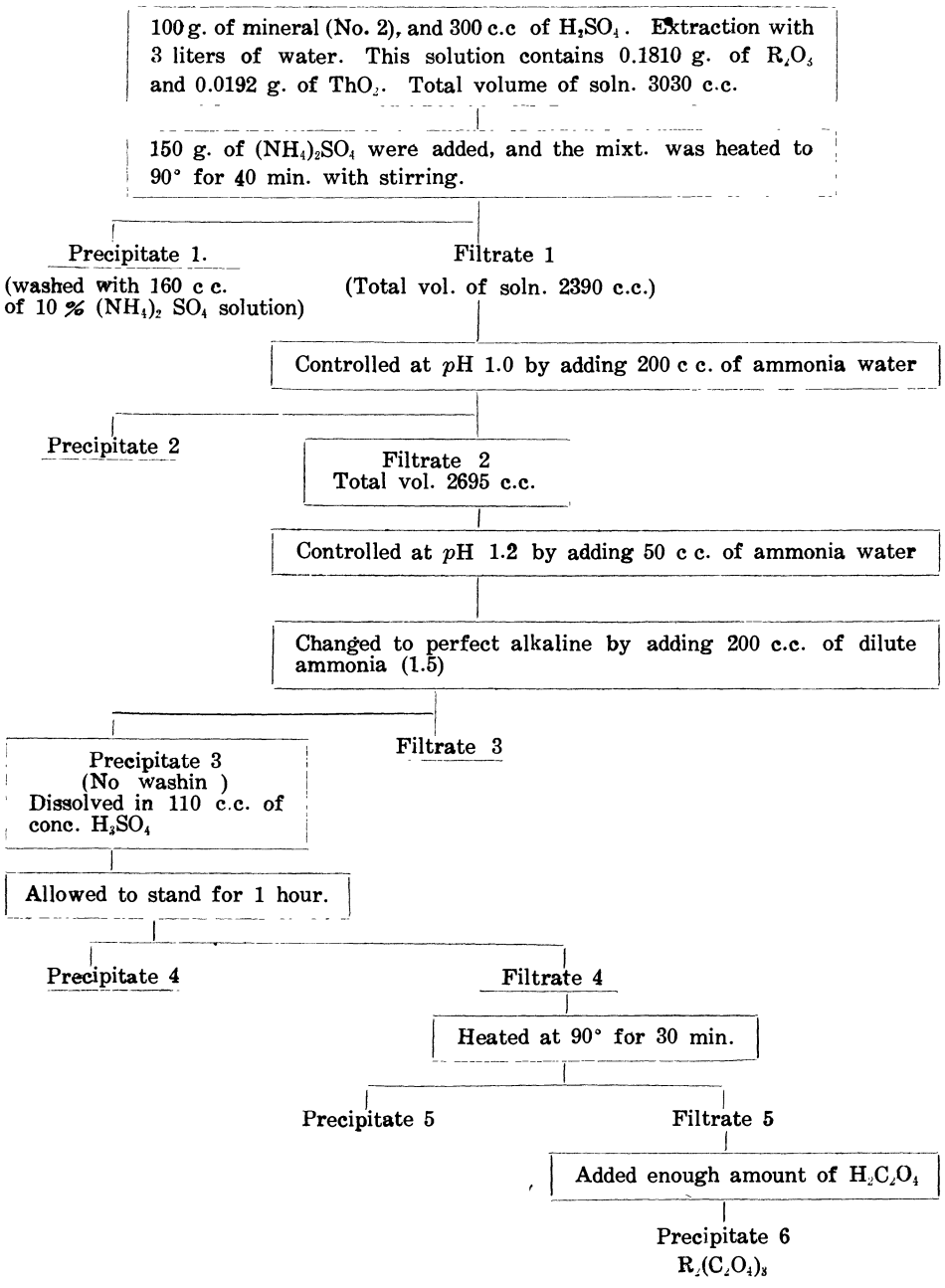
In the past, method (a), using ammonia or magnesia, was used in industry. Method (b) has been adopted recentry, especially for the treatment of monazite of low thorium content. The author carried out a few experiments on the two methods. As the results, it is seen that in separating thorium from rare earths by fractional precipitation with ammonia, when *p*H is controlled at 1.0, precipitate of thorium compound having the purity ($ThO_2/ThO_2+R_2O_3$) of 93% was obtained (yield 60%). When the *p*H was controlled at 1,2, the purity was 86% and yield 80%. However, the composition of the precipitate changes remarkably due to slight change of *p*H. The precipitate is voluminous, and is difficult to filter.

In the method by the adition of sodium sulphate or sodium chloride and sulphuric acid, the precipitate was not difficult to filter but the efficiency for separation from one another was considerably inferior to the above method.

3. Separation of rare earths from the extracted solution as ammonium rare earths sulphate compound. The author tried to separate rare earths from the extracted solution as ammonium rare earths sulphate compound in order to improve the defects of the method of fractional precipition by ammonia. This compound is a pink crystal and is produced ahead of thorium phosphate when the concentration of the extracted solution is above a certain value. Its composition war found to be $(NH_4)_2SO_4 \cdot R_2(SO_4)_3 8H_2O$. This double compound is produced in larger amounts at higher temperature than at room temperature. The precipitate which is produced at higher temperature is in the form of small particles and is difficult to filter. Therefore, it is better to keep the solution at room temperature and make the precipitate grow as much as possible, and then to precipitate the remaining rare earths as small particles at higher temperature. About 63% of rare earths, which is free from thorium, can be separated. Considering that 37% of rare earth remains in the solution, the author attempted to separate th

rare earths by adding more ammonium sulphate and heating to 90°C. A brilliant white precipitate was formed but it contained considerable amounts of thorium. The relative concentration of thorium in the filtrate, after the recovery of 63% rare earths, has been raised. When

Table 2.



fractional precipitation by adding ammonia to the filtrate was done and *p*H of the solution was controlled, a white isinglasslike precipitate was prduced. It was almost free from cerium. The filtrate from the above precipitate was controlled to *p*H 1.2, and it produced a white amorphous precipitate, in which the ratio $ThO_2/ThO_2+R_2O_3$ was 0.27. Then this precipitate was filtered off, and the filtrate was controlled to *p*H 2.0. It produced a white precipitate, which contained no thorium. Therefore the above procedure is simple and gives better results than a method of direct fractional precipitation by addition of ammonia. It can be shown as follows (Table 2).

The weight and composition of obtained precipitates are shown in Table 3.

Table 3.

No. of ppt.	Weight of ppt.	Composition	R_2O_3 in the ppt.	$ThO_2/ThO_2+R_2O_3$	Rate of recovery
1	62.5 g.	$(NH_4)_2SO_4R_2(SO_4)_3$ $8H_2O$	25.4 g.	0 %	51.9 %
2	158 g.	Th-phosphate & R-hydroxide	1.5 g.	66.7	3.1
3	67 g.	Same to the above	2.97 g.	29.9	6.05
4	37 g.	$(NH_4)_2SO_4R_2(SO_4)_3$ $8H_2O$	15.1	0	30.9
5	4 g.	Same to the above	1.6	0	3.3
6		$R_2(C_2O_4)_3$	1.4	0	2.8

4. Separation of cerium from the rare earths ammonium sulphate double salt. Cerium is present in the double compound only in trivalent cerous form. In solution this may be oxidized to tetravalent ceric from, by ammonium persulphate, permanganate etc.

When the acidity of the resulting solution is decreased by adding dilute ammonia, a yellow precipitate of ceric-oxy-sulphate forms. The author tried to follow this plan to separate cerium from the other rare earths and to investigate the quantities of the reagent required for the most favorable separation. In the first investigation, experiments were performed to determine the quantities of ammonium persulphate necessary to completely oxidize the cerous cerium to ceric. According to the rerults of the experiments, the quantity of ammonium persulphate required is seven times the theoretical quantity. In the investigation in which the oxidized cerium was precipitated by ammonia, the relation of (1) the quantity of ammonia, (2) the purity of the precipitate and (3) the percentage of recovered cerium, was studied.

Experiment performed: The solution used in this investigation had the composition shown in Table 4. To 25 c.c. of this solution various quantities (25.0, 25.5, 26.0, 26.2, 26.5 and 27.0 c.c.) of 1.022N ammonia

were added. The mixtures were permitted to stand overnight and then filtered. The precipitates were analysed immediately without washing. The results are shown in Table 5.

Table 4

$C^{\cdots} + Ce^{\cdots\cdot}$	8.0 mg/c.c.
$Ce^{\cdots\cdot}$	7.4 mg/c.c.
Oxidizing rate	92.5%
R_2O_3	16.2 mg/c.c.
Free acidity	2.49N.

Table 5.

No.	1	2	3	4	5	6
Added amount of ammonia (c.c.)	24.0	25.5	26.0	26.2	26.5	27.0
Yield of Ce (%)	65	69	69.5	75	87	100
Purity of Ce	86	87	93	95	87	69
*p*H	2.07	2.13				

As is evident from this table, the relation of purity and yield of cerium was not strictly reverse, but a point of maximum of purity exists when a certain definite amount of ammonia was added.

Next the author tried the following experiment in order to reexamine "this point" and to investigate the effect of adding smaller quantities of more coucentrated ammonia solution. In this experiment the precipitates were washed with distilled water. A saturated aqueous solution of the double compound was prepared and a few drops of sulphuric acid were added to prevent hydrolysis. It contained 93.7 mg. of CeO_2 per 10 c.c. with a free acidity of 1.64N. Ammonia solution (1.96N) was added into 25 c.c. of the solution drop by drop. When about 21 c.c. of ammonia was added to the first portion, precipitates began to appear. Similar experiments were performed using 21.10, 21.55, 21.86, 22.00, 22.40 and 22.70 c.c. of ammonia respectively. After the ammonia was added, the samples were allowed to stand for 1 day and then filtered. The results of the experiments are shown in Table 6.

Table 6.

No.	1	2	3	4	5	6
Added amount of ammonia (c.c.)	21.10	21.55	21.86	22.00	22.40	22.70
Yield of Ce (%)	66.0	66.5	72.2	77.8	91 4	99.3
Purity of Ce (%)	93.0	94.4	96.7	95.2	94.1	83.2
*p*H	1.82	1.84	1.87	2.12		5.90
Colour of soln.	yellow	yellow	⊙colourless	,,	,,	,,

⊙ The filtrate of the solution of ammonium rare earths sulphate, from which 70% of cerium had been separated, contained 30 % of cerium notwithstanding the fact that the solution was colourless, but when sulphuric acid was added to the colourless solution, distinct colour appeared.

Summary. (1) The rare earths, free from thorium, could be separated as the earths sulphate double compound (yield 93%).

(2) The method of separating thorium from the filtrate, which was obtained by separating about 63% of rare earths salt from the extracted solution, gives better result than a method of direct fractional precipitation from the extracted solution.

(3) Cerium can be separated from a solution as rare earths ammonium double compound with a purity of 92—96% (yield 70—75%).

(4) In the separation of cerium, a maximum point of purity is obtained when sufficient quantity of ammonia is added just to remove the colour of Ce ion from the solution. The purity and yield of cerium is not strictly in an inverse proportion, but a point of maximum purity of precipitate is obtained when a certain definite amount of ammonia is added.

In conclusion the author wishes to express his hearty thanks to Prof. Kenjiro Kimura and Dr. K. Kuroda of the Tokyo University, and Director S. Tashiro of the Noguchi Institute for their kind guidance in the course of this study.

Chemical Institute, Faculty of Science, Tokyo University
and Noguchi Institute.

Die Polarographische Bestimmung des Molybdations.

von Kazuo SAITO.

(Eingegangen am 6, Juli 1948.)

Die polarographische Reduktion des Molybdations its bisher nur wenig untersucht worden. F. A. Uhl[1] gibt an, dass Molybodän in milchsaurer Lösung zwei Stromstufen gibt, von denen die zweite zur quantitativen Bestimmung geeignet sei. Aber nach R. Höltje und R. Geyer[2] kommt das Uhlsche Verfahlen für die praktische Analyse kaum in Frage; sie haben die polarographische Reduktion des Molybodäns in mancher sauren Lösungen geprüft. Ausserdem haben G. Thanheiser, J. Willem[3] und M. v. Stackelberg und seine Mitarbeiter[4] auch über dieses Problem gearbeitet.

Ich habe das polarographische Studium des Molybdations durchgeführt, um näher kennen zu lernen, ob die Stromspannungskurve des Molybdäns auf die quantitative Analyse dieses Elementes angewandt werden kann. Da das Ziel dieser Arbeit die analytische Auswertung des Polarogramms ist, handelt es sich hier nicht um die elektrochemische Natur der Stufenwelle

Die Grundlösung. Für den praktischen Gebrauch ist einfache Zusammensetzung wünschenswert. Von der grossen Zahl der Grundlösungen ist die Nitrat-Lactat Lösung nützlich. Uhl hat eine Lösung von solcher Art gegeben, aber sein Rezept scheint mir für die quantitativen Zwecke nicht befriedigend. Meiner Erfahrung nach ist die folgende Zusammensetzuug geeignet.

Grundlösung 1.

Ammoniumnitrat	2M	40ccm	Auf 100ccm aufgefüllt (A.P. +0.26 zu Normal Kalomel Elektrode)
Salpetersäure	6N	10ccm	
Milchsäure	2N	10ccm	
Molybdat Lösung			

In Abb. 1 wird das Polarogramm mit der Grundlösung 1 aufgenommen angegeben. In dieser ist die Stufenhöhe proportional der Konzentration des Molybdations.

Die Hinzufügung des Oxalations ist zwar für die Proportionalität der Höhe nicht unentbehrlich, aber bei der Gegenwart des Phosphat- bzw.

(1) F.A. Uhl: *Z. Anal. Chem.*, **110** (1937) 102.
(2) R. Höltje & J. Geyer: *Z. Anorg. Allg. Chem.* **246** (1941) 258.
(3) G. Thanheiser & R. Willems: *Arch. Eisenhüttenwes.* **13** (1940) 73.
(4) M.v. Stackelberg, P. Klinger, W. Koch & E. Krath: *Techn. Mitt. Krupp* **6** (1939) 75.

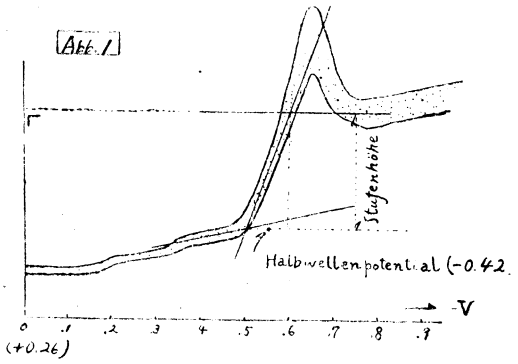


Abb. 1.

Germanations hindert es die Fällung des entsprechenden Heteropolymolybdats, was im Falle der Anwendung dieser Methode auf die Analyse jener Ionen sehr vorteilhaft ist. Daher wird die Grundlösung der folgenden Zusammensetzung empfohlen.

Grundlösung 2.

Ammoniumnitrat	2M	40ccm	Auf 100ccm aufgefüllt (A.P. +0.28 zu Normal Kalomel Elektrode)
Salpetersäure	6N	10ccm	
Milchsäure	2N	10ccm	
Oxalsäure 2aq.		2.5g	
Molybdat Lösung			

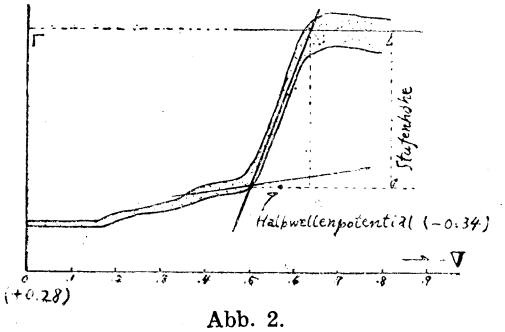


Abb. 2.

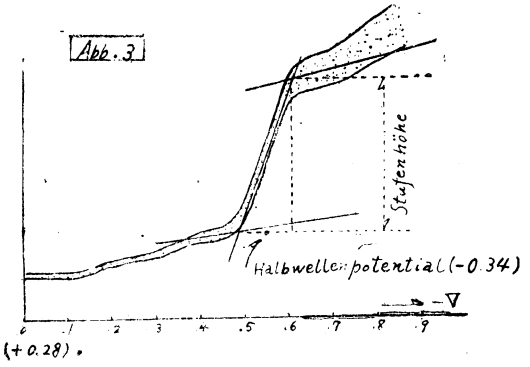


Abb. 3.

In Abb. 2 wird das Polarogramm mit dieser Grugdlösung aufgenommen gezeigt. Die Menge der Salpetersäure (6N) muss mehr als 5ccm in 100ccm der Lösung betragen (0.3N). Wenn es nicht so ist, vermindert sich die Stufenhöhe des Molybdäns und wird die Proportionalität verloren. Ist der Salpetersäuregehalt zn gross, wird eine Stufenkurve, wie in Abb. 3 gezeigt, gewonnen; aber die Proportionalität wird aufrechterhalten. Gelatin, Tylose oder anderes Kolloid soll nicht dasein.

Arbeitsweise und Versuchsergebnisse. Für die Herstellung der Normallösung brauchen wir das Ammoniummolybdat auf dem Markt. (10mg Mo/ccm, 1mg Mo/ccm). In ein 100ccm Becherglas wird die Normallösung (Probelösung) mit einer Messpipette getan und mit 15ccm Wasser versetzt. Hierauf wird Oxalsäure hinzugesetzt und mit Hilfe von geringem Erwärmen gelöst. Nach Zusatz von Ammoniumnitrat und Salpetersäure wird die Lösung gekühlt und in einen 100ccm Kolben gegossen. Dann wird sie mit Milchsäure versetzt und auf 100ccm aufgefüllt. Aus dem Kolben werden 10ccm mit Pipette durchgezogen und in ein kleines Becherglas gegossen. Die Vertreibung des Sauerstoffes ist nicht nötig.

Die Polarogramme wurden mit einem Polarographen des "Yanagimoto"s aufgenommen. Eine Kapillare mit einer Tropfengeschwindigkit von 1 Tröpfchen in 3 Sekunden ist für die Kathode geeignet. Die Quecksilberhöhe muss während der gesamten Arbeiten konstant bleiben. Nach dem Aufnehmen des Polarogramms der Probelösung wird ein wenig Normallösung mit einer Messpipette hinzugesetzt und sie noch einmal polarographiert. Die Menge des anfänglich hinzugefügten Molybdäns wird nach der Stufenhöhen der zwei Polarogramme berechnet. Die Ergebnisse zeigen sich in Table 1. Die Maximumempfindlichkeit des Galvanometers ist 4×10^{-8}.

Tabelle 1.

No.	Gemenge des Mo genommen	Empf. Galvs.	Oxalsäure	Gemenge des Mo gefunde
1	0.60 mg	1/100	--	0 61 mg
2	1.00	,,	--	0.99
3	1.00	,,	--	0.98
4	0.50	1/50	+	0.51
5	1.00	1/50	+	1.04
6	0.46	1/20	+	0.46
7	0.46	1/50	+	0.46
8	1.10	1/100	+	1.10
9	1.10	,,	+	1.16
10	0.31	1/20	+	0.36
11	0.11	1/20	+	0.12

Je höher die Empfindlichkeit des Galvanometers, desto undeutlicher die Krümmung der Stromspannungskurve. Daher ist diese

Methode für die genaue Bestimmung von Molybdän weniger als O. 1mg nicht wünschenswert. Die Form dieses Polarogramms verändert sich nicht ohne Rücksicht auf den Vorhandensein der geringen Mengen von Phosphor bzw. Germanium; daher kann die obige Methode auf die quantitative Analyse solches Elementes angewandt werden.

Zusammenfassung. Ein kleines Gemenge des Molybdäns kann mit Hilfe von einer neuen Grundlösung, die aus Ammoniumnitrat, Salpetersäure, Milchsäure und Oxalsäure besteht, durch polarographische Methode genau bestimmt werden. Der Prozess ist verhältnismässig leicht und erfordert nicht lange Zeit

Zum Schluss möchte ich Herrn Professor Kenjiro Kimura für seine freundliche Anleitung und Ratschläge bei der vorliegenden Arbeit meinen herzlichen Dank aussprechen.

Chemisches Institut der Naturwissenschaftlichen Fakultät, Universität zu Tokio.

On the Equilibrium of the Radioactive Elements in the Hydrosphere. I.

By Kazuo KURODA and Yuji YOKOYAMA.

(Received June 19, 1948.)

Introduction. This is the first of a projected series of studies on the equilibrium of the radioactive elements in the hydrosphere. It is well known that many natural waters, particularly hot springs and mineral springs, contain quite an appreciable amounts of radium and radon (radium emanation), and the equilibrium relationships between these elements were discussed by many investigators[1]. However, other radioactive elements are very seldom determined in the analyses of natural waters and hence very little is known about their distribution in natural waters. As a preliminary step in the thorough investigation on the occurrence of radioactive elements in the hydrosphere, the methods of determining radon were studied by the present authors and a satisfactory procedure was developed. Instead of I. M. fontactoscope, which is widely used in this country, the present authors also used a Lauritsen-type K. Y. fontactoscope newly devised and constructed in our laboratory. Radon is determined by this new apparatus very quickly and accurately.

As a first contribution, the occurrence of radioactive elements in the mineral waters, the rain water, and the fumarole vapour of the Volcano

Hakone was studied and the results obtained are here presented. The radioactive elements already determined by the present authors are as follows. (Table 1);

Table 1.

Name	Symbol	Isotope	Half Period	Radiation
Radium	Ra	Ra	1590 yrs.	α
Radon (Radium emanation)	Rn	Rn	3.825 days	α
Radium A	Ra A	Po	3.05 min.	α
Radium B	Ra B	Pb	26.8 ,,	$\beta(\gamma)$
Radium C	Ra C	Bi	19.7 ,,	99.97%β and α
Radium F (Pelonium)	Ra F (Po)	Po	140 days	α
Radiothorium	RdTh	Th	1.90 yrs.	α
Thorium X	ThX	Ra	3.64 days	α
Thoron (Thorium emanation)	Tn	Rn	54.5 sec.	α
Thorium A	ThA	Po	0.14 ,,	α
Thorium B	ThB	Pb	10.6 hrs.	β and γ

These radioactive elements are present in rocks and minerals in the equilibrium amounts to uranium and thorium, excepting some secondary minerals newly formed, and hence it is meaningless to determine their amounts in rocks and minerals separately. On the other hand, these elements are present in the hydrosphere in quite irregular proportions and they are present in the equilibrium proportions only exceptionally. It is considered, therefore, that we can solve some geochemically interesting problems by the study of these "disturbances" of the equilibrium of the radioactive elements in the hydrosphere.

I. Apparatus. For the determination of radon, a Lauritsen-type K. Y. fontactoscope was used. (Fig 1a). This apparatus was planned by the authors. The radon container (Fig. 1b) is made of brass and

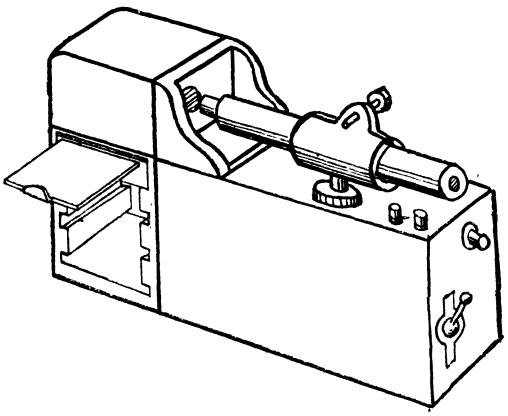


Fig. 1*a*. Lauritsen-type K.Y. Fontactoscope.

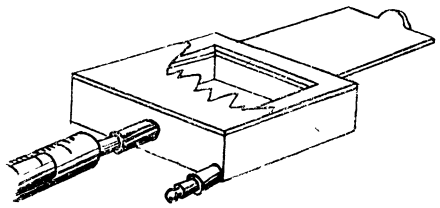


Fig. 1*b*. Radon Container.

its size is 50 mm × 50 mm × 10 mm. The water samples (0.5-several c. c.) are taken by the injectors, shaken in the radon container, and the intensity of the α ray is measured through 7 μ aluminium foils of radon container and of ionization chamber. The accuracy of the measurements was compared with that of I. M. fontactoscope and the satisfactory agreements were obtained. For the determination of other elements, such as radium, thorium, thorium X, polonium, radium A, B, C etc., these elements were co-precipitated with the suitable carriers, and the radioactivity of the powdered samples was measured by the Lauritsen-electroscope under the suitable conditions, as is described in the following section.

II. Equilibrium between Radon and its Decay Products (Radium A, Radium B and Radium C) in the Hydrosphere. The authors have intended the rapid determination of radon in natural waters by the measurement of the intensity of β ray from the decay products of radon, and found that the decay products are contained in most radioactive springs only in very small proportions, when the springs issued; Their amounts increase after the spring water issued, and the equilibrium values are obtained after about three hours. Why the decay products of radon are almost absent in fresh spring waters? The reason for this is considered to be as follows: The mineral water dissolved the radon gas at the "source of radon" near the surface of the earth, and it may be supposed that the decay products of radon were not dissolved in the mineral water at the time. As this "source of radon" is considered to be located at the places not so deep in the earth, it may be supposed that the sufficient time did not elapsed to establish the equilibrium between radon and its decay products. According to this hypothesis, the time (T) elapsed since the radon dissolved in the mineral water at the "source of radon" until the mineral water issued was calculated and the following results were obtained. (Table 2).

Table 2.

Name of Springs	Radon Content (Mache)	T (min.)
A 3	2.7	45
A 4	64	15
A 6	154	10
A 8	1580	10
A49	3700	2

These results are not contradictory to the geological observations, and to the geochemical observations on the variations of the radon content of these mineral springs after the rain or snow, as it is already reported in the previous paper[1].

III. Ratio of Thoron to Radon in Natural Waters. As the half period of thoron is very short, its accurate determination is rather difficult and hence very little is known about the distribution of thoron in natural waters. The present authors have measured the thoron content of a number of radioactive springs, and found that the spring B7, in Masutomi, Yamanashi Prefecture, contains appreciable amounts of thoron, although its radon content is low. (Fig. 2.) It seems that the larger

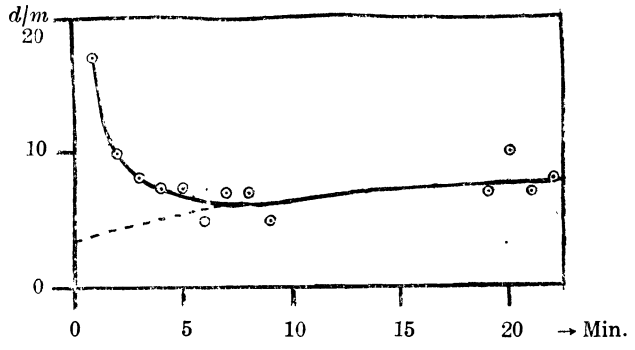


Fig. 2.
Decay Curve of Tn and Rn of the Spring B7-Gas.

the velocity and the amount of flow of mineral springs, the larger is the ratio of thoron content to radon content.

A 20–40 c.c. portion of sample water was taken with the injector quickly, and the radioactivity was measured with the I. M. fontactoscope. The thoron content of a number of mineral springs and gas of Masutomi is shown in Table 3.

Table 3.

Name of Springs	Thoron Content (Mache)	Radon Content (Mache)
B7	95	
	82	
	85	6.27
	67	
	84	
A3	15	2.2
A3′	16	5.9
A3″	10	——
A1	10	— —
A49	absent	about 5000
A2	,,	2–4
A6	,,	about 100

(1) K. Kuroda, this Bulletin, **19** (1944), 33.

Table 3.—(*Continued*).

Name of Springs	Thoron Content (Mache)	Radon Content (Mache)
B7 Gas	107 96 103 94	19.5
A1 Gas	10	——
A49 ,,	absent	——
B8 ,,	,,	——

IV. Isotopes of Radium in Natural waters. The authors have studied the rapid method of the determination of radium in natural waters, and found that the mineral waters of Masutomi contain also thorium X. Radium and thorium X were coprecipitated together with barium sulphate from 1 litre of the mineral water, and the radioactivity of the powdered precipitate was measured with the Lauritsen electroscope. The radioactivity diminishes slowly for several days, according to the presence of thorium X. Its half period is about three days. The radioactivity due to radium is measured after the radioactivity due to thorium X disappeared. The amount of radium and thorium X is calculated from the curves of the change of radioactivity as is shown in Fig. 3. The thorium X and radium content of mineral springs of Masutomi is shown in Table 4.

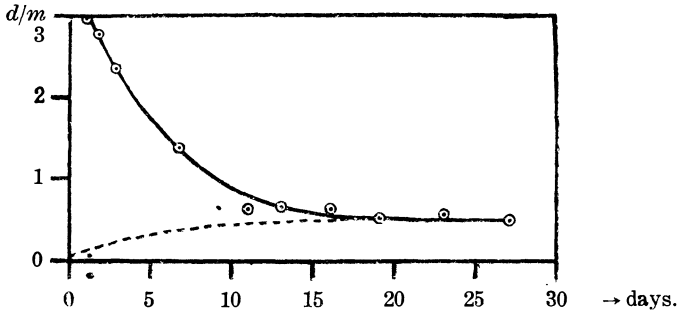


Fig. 3.
Decay Curve of Th X and Ra of the Spring B7.

Table 4.

Name of Springs	Radium Content (10^{-12} g/l)		Thorium X Content (10^{-12} C/l)	
	Aug. 1947	Feb. 1948	Aug. 1947	Feb. 1948
A1	28	23	111	104
A2	37		191	
A3	32	26	149	128
A4′	25	23	74	65
A5	76	52	184	160
A6	23	11	64	29
A7				
A8	14		10	
A9				
A49	8	6	12	2
A50	17		18	
A51	13		68	

Table 4.—(*Continued*)

Name of Springs	Radium Content (10^{-12} g/l)		Thorium X Content (10^{-12} C/l)	
	Aug. 1947	Feb 1948	Aug. 1947	Feb 1948
B1	9		4	
B2′	less than 0.5		less than 0.5	
B4	3		,,	
B5	19		83	
B6	7		less than 0.5	
B7	31	27	320	340
B8				
B9	9		12	
C1	6		12	
C2	8		3	
C3	less than 0.5		3	
C4	2		4	
Dα	2		less than 0.5	
Dβ	less than 0.5		,,	
Dγ	3		,,	
E1	62		72	

The spring B7 showed the highest thorium X content. It is the highest value ever reported in the world. In the mineral springs of Masutomi, the following tendency was noted, namely: ··· "the higher the water temperature and the larger the amount of flow, the larger is the ratio of thorium X to radium".

This fact is satisfactorily understood, assuming that the source of radium and thorium X is located at a considerable depth in the earth. (As already mentioned, the source of radon is considered to be located quite near the earth's surface). It may be supposed that the considerable amount of thorium X decays when the spring water flows from the source of radium and thorium X to the earth's surface, as the half period of thorium X is short (3.64 days), whereas radium does not decay so much, as its half period is considerably long (1590 years). The determination of actinium X was also tried, and the results will be reported later in detail.

Summary. The equilibrium relationships of the radioactive elements in the hydrosphere was studied. The radium, radon, radium A, radium B, radium C, radium F (polonium), thorium X, thoron, and thorium B content of mineral springs of Masutomi was estimated, and discussed from geochemical point of view. It was found that spring B7 shows the high content of thorium X and thoron. Spring A49, on the other hand, showed the high content of radon and polonium. It was also found that the decay products of radon are contained in fresh mineral springs in

considerably lower amounts compared with those expected from the radon contents.

The authors take this opportunity of heartily thanking Prof. Kenjiro Kimura for his kind guidance in the course of this study. The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which our thanks are due.

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On the Equilibrium of the Radioactive Elements in the Hydrosphere. II.

By Kazuo KURODA and Yuji YOKOYAMA.

(Received June 19, 1948).

V. Radioactivity of the Rain Water. It was discovered in 1903 by C. T. R. Wilson[1], that the fresh rain water is radioactive, and its half period is about 30 minutes. The radioactivity of the rain water was measured by many investigators since then, and it is believed that the radioactivity is due to the presence of radium B and radium C in the fresh rain water. It is supposed that radium A (positively charged) formed from the radon in the air, is adsorbed by the small particles of rain water (negatively charged). The present authors have measured the radioactivity of the rain water since the summer of 1947, at Masutomi, Yamanashi prefecture, and in Tokyo. Several c. c. of the rain water, taken very quickly, were evaporated, and the radioactivity of the residue was measured with the Lauritsen electroscope. The ionization current diminished slowly at first for 10 to 30 minutes, and after about 40 minutes it diminished quickly almost according to the exponential curves, and the half period of that stage was about 34 minutes. A. Gockel and T. Wulf[2] reported, contrarily, that it diminishes quickly at first and described that the fresh rain water contains much radium C and little radium B at first. The opposite result was obtained, however, by the experiment of the present authors. It is considered that it is improbable that the

(1) C. T. R. Wilson, *Proc. of the Cambridge Philos. Soc.*, **12**, II (1903), 85.
(2) A. Gockel and T. Wulf, *Phys. Z.* **9** (1908), 907.

amount of radium C is larger than that of radium B, if the radioactivity of the rain water is due to the adsorption of radium A, as the half period of radium C is shorter than that of radium B. The results of the measurements are shown in Table 5 a and b.

Table 5*a*. Measurements at Masutomi.

Date	June 15	June 15	Aug 17	Aug. 17	Aug. 17
Time	15.14	16.05	13.30	15.16	16.40
Time needed for sampling	60 min.	30 min.	60 min.	40 min.	20 min.
Sample taken	2.7 c.c	9 c.c	18 c.c.	18 c.c.	20 c.c.
Radium C Content ($\times 10^{-10}$ C/1)	300	340	190	150	180
Remark			thunder rain		

Table 5*b*. Measurements at Tokyo.

Date	Aug. 27	Aug. 27	Aug. 30	Sept. 2	Oct. 6	Nov. 20
Time	14.44	15.02	15.46	14.02	15.30	12.29
Time needed for sampling	15 min.	10 min.	18 min.	11 min.	10 min.	10 min.
Sample taken	24 c.c.	12 c.c.	20 c.c.	10 c.c.	2 c.c.	1 c.c.
Radium C Content ($\times 10^{-10}$C/1)	50	65	250	150	90	80
Remark	thunder rain		thunder rain	thunder rain		

The rain water shows the unexpectedly high content of the radioactive elements, compared with that of the air which is about $20\text{–}300 \times 10^{-15}$C/1, and that of ground water, which is usually less than 1×10^{-10}C/1. It is rather difficult to compare the results of the measurements of the radioactivity by many investigators in other countries, as these measurements were carried out very early, and mostly before the confirmation of the units of the concentration of the radioactive elements. A. Goçkel obtained the values of 0.64–7.5 Mache/l ($2\text{—}30 \times 10^{-10}$C/1), and they are very low compared with those obtained by the authors in this time. Moreover, the investigators in other countries reported, without exception, that the thunder rain shows the higher radioactivity than the ordinary rain water, but the present authors could not find out such difference. It must be noted that in the old measurements in other countries, considerably long time was needed to collect the rain water, and the decay of radium C in this interval is not taken into consideration. In our experiment, the sampling and the evaporation were carried out as quickly as possible, and the correction for the decay of radium C in this interval was given. The rain water at Masutomi, where many radioactive springs issue, showed the higher content of radium C than that of Tokyo.

VI. Radioactivity of the Fumarole Vapour of the Volcano Hakone. It was found by the present authors that the fumarole-vapour of

the Volcano Iōyama (Sulphur Mountain) at Hakone is also slightly radioactive. This radioactivity is considered to be due to the presence of radium A, its half period being about three minutes. The fumarole vapour was collected with a glass funnel and a long glass tube cooled by snow. The water obtained like this was evaporated up very quickly and the radioactivity of the residue was measured with the Lauritsen electroscope. The sampling must be finished very quickly, as the half period of radium A is very short. Table 6. shows the result of the experiments.

Table 6.

The radioactivity of the fumarole vapour of the Volcano Hakone due to the presence of Radium A.

The amount of water sample: 1 c. c.
The time needed for sampling: 40 seconds.

Time (Minutes)	Radioactivity (Div./Min.)
1	0.25
2	0.17
3	0.12
4	0.12
5	0.07
6	0.02
7	0.07
8	0.02
10	0.02
13	0.00

The radium A content of the water of the fumarole vapour was calculated from the data of above-mentioned experiment, and the following value was obtained.
The radium A content $= 230 \times 10^{-10}$ Curie/1.

When the longer time was needed for sampling, we could not observe the radioactivity of radium A, and the very weak radioactivity due to radium C was detected. The radium C content was estimated to be as follows.

Table 7.

	The amount of sample	Time needed for sampling	Radioactivity	
			Time (min.)	Ionization current (Div./min)
No 1	10 c c.	2 hours	22	0.02
			42	0.01
No. 2	5.6 c.c.	5 minutes	17	0.06
			27	0.07

The radium C content
No. 1 1.5×10^{-10} Curie/1.
No. 2 9.5×10^{-10} Curie/1.

The radon content of the gas ejected frem the fumaroles was also measured and the results are shown in Table 8.

Table 8. The radon content of the fumarole gas of the Volcano Ioyama, Hakone.

	Radon content (94°C, 660 mm)	Radon content (0°C, 760 mm)
No. 1	5.5 Mache 20×10^{-10} C/1	8.6 Mache 31×10^{-10} C/1
No. 2	6 7 ,, 24×10^{-10} C/1	10 ,, 37×10^{-10} C/1

The experimental data obtained above are very satisfactorily explained assuming that the radium A is adsorbed completely by the fumarole vapour. If we assume that the radium A, formed from radon, is adsorbed completely by the water particles, and the contacting time of fumarole gas and vapour is t seconds, the following relation will be obtained-:

$$[Ra\ A] = [Rn] \times \lambda_{RaA} \times t \times \frac{1000}{w} \qquad (1)$$

w : The amount of water (g) obtained from 1 litre of the fumarole gas.
$[Ra\ A]$: The concentration of RaA in water. Curie/1.
$[Rn]$: The concentration of Rn in gas. Curie/1.
λ_{RaA} : Disintegration constant of RaA.

If we assume that $[Rn] = 30\times10^{-10}$, $t = 0.5$ seconds, and $w = 0.2\ g.$, the following value will be obtained for RaA. This is almost equal to the observed velue. (Table 9).

Table 9.

Ra A	
Calculated	Observed
300×10^{-10} Curie/1	230×10^{-10} Curie/1

The 230×10^{-10} Curie per litre of radium A will disintegrate and about 10×10^{-10} Curie per litre of radium C will be formed in about thirty minutes. This value is almost equal to the observed value of radium C shown in Table 7.

VII. Geochemistry of Polonium in the Hydrosphere. It was found recently by the present authors that some mineral springs in Masutomi contain considerable amounts of polonium (radium F), and the polonium content of a number of mineral springs was estimated. Polonium was separated from the mineral water as polonium sulphide, a small amount of lead compound being added as the carrier. Radium A, radium B,

thorium B etc. also precipitated, but their radioactivlty disappeared in several days, as their half periods are short, and the radioactivity due to polonium remained. Its half period was found to be about 140 days. The radioactivity was compared with that of polonium samples extracted from known amounts of pitchblende, and the polonium content of the mineral springs was calculated. The polonium content of mineral springs of Masutomi is shown in Table 10.

Table 10.

Name	Polonium content (10^{-10} C/L)
A49	3.9
A9	0.20
B4	0.10
B9	0.05
A1	less than 0.02
A3	,,
A4′	,,
B7	,,

Polonium was detected without exception in the mineral springs containing large amounts of radon. The polonium content of spring A 49 seems to be the highest in the world. It is very interesting that polonium in mineral springs shows some peculiar reactions. It was found, for example, that polonium is not precipitated by ammonia from the mineral water, although the polonium samples, which was obtained by precipitating as sulphide, are precipitated as hydroxide by ammonia or sodium hydroxide solution. These chemical reactions of polonium in mineral springs are now being studied in detail and the results will be reported later.

VIII. Radium A, Radium B, Radium C, and Thorium B Contents of Mineral Spring of Masutomi. As is already described in section II, the radium A,radium B and radium C contents of fresh mineral waters are considerably low, compared with the values expected from their radon contents.

The thorium B content of a number of mineral springs of Masutomi was also estimated recently. The results of these measurements are shown in Table 11.

Table 11.

Name	RaA	RaB	RaC	ThB
Unit		10^{-10} C/1		10^{-12} C/1
Date		June 1947		Feb. 1948
A1				92
A3		6.5	3.5	115
A4′		55	10.5	80
A6		80	10	80
A8	4400	800	100	
A49	4500	140	3	20
B7				280

Snmmary.

(1) The equilibrium relationships of the radioactive elements in the hydrosphere were studied.

(2) The radioactivity of the rain water and the fumarole vapour was measured.

The authors take this opportunity of heartily thanking to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which our thanks are due.

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Studies on Synthetic Polyamides (VI)[1] Dimeric ε-Caprolactam.

By Kôhei HOSHINO.

(Received March 12, 1946.)

ε-Caprolactam $HN(CH_2)_5CO$ (I) (m. p. 68°) on being heated in an autoclave, reacts with itself and yields linear polycapramide — $HN(CH_2)_5CO \cdot HN(CH_2)_5CO \cdot HN(CH_2)_5CO$ — (II) (m. p. 210–220°)[2] and a small quantity (below 0.01%) of fluffy byproduct sublimes to adhere to the upper part of the autoclave. The sublimate is slightly soluble in water and alcohol, insoluble in ether and petroleum ether, and soluble in formamide and hot water from which it separates as a microcrystalline powder melting at 341–342° on cooling. Its analytical composition agrees very closely with that required for the structural unit — $NH(CH_2)_5CO$—.

Anal. (Submicro-Kjeldhal). Found: N, 12.31. Calculated for $C_6H_{11}ON$: N, 12.38.

It is quantitatively hydrolyzed in six hours by boiling with concentrated hydrochloric acid to ε-aminocaproic acid. This was identified by conversion into the benzoyl derivative (melting point and mixed melting point, 78–80°), and by measurement of the weight increase of hydrochloride, 48.6% (calculated for the conversion from $(HN(CH_2)_5CO)_n$ (III) to n

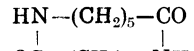
(1) The fifth paper: this Bulletin, **19** (1944), 171.

(2) Hosino and Noisiki: this Bulletin, **18** (1943), 105.

[$HCl \cdot H_2N(CH_2)_5COOH$]: 48.2%). By oxidizing the sample with concentrated nitric acid, adipic acid $HOOC(CH_2)_4COOH$ was obtained.

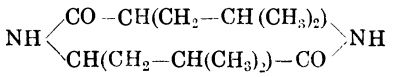
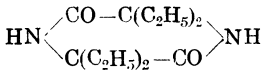
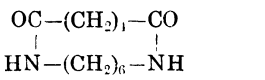
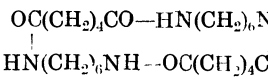
On heating the sample in a sealed tube at 280° with two hundred-parts of water for five hours, it yielded a transparent solution, then by continued heating in an open tube, it was converted to a polyamide melting at 215°, i. e. the linear polycapramide (II). By these facts, it is proved that it retains the structural unit of ε-caprolactam.

This compound is sufficiently soluble in camphor to determine the molecular weight when the quantity of the solvent is increased to about a hundred fold of the solute. The value obtained of n corresponding to the formula (III) was 2. Therefore its structure may be represented by the formula (IV), i. e. neutral cyclic dimeric capramide (a 14-membered ring compound).



(IV)

It is conceivable that the high melting point of this compound is due to two amide groups of high molecular cohesion in one ring. The following compounds (V), (VI), (VII) and (VIII) are some examples of substances with similar structure.

Cyclic amide	Ring size	Formula	M.p., °C.
3,6-Dioxo-2,5-diisobutyl-piperazine (V) (lactam of leucylleucine)	6		271[3]
3,6-Dioxo-2,2,5,5-tetraethyl-piperazine (VI)	6		346[3]
Neutral cyclic monomeric hexamethylene adipamide (VII)	14		248[4]
Neutral cyclic dimeric hexamethylene adipamide (VIII)	28		238[4]

Summary.

The fluffy sublimate (m. p. 341–342°), byproduct of the polymerization of ε-caprolactam, is shown to be neutral cyclic dimeric capramide (IV) (a 14-membered ring compound).

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(3) Beilsteins Handbuch der Org. Chem. Bd. 24. Ergänzbd. 311-312.
(4) Greenewalt, U.S.P. 2,241,323.

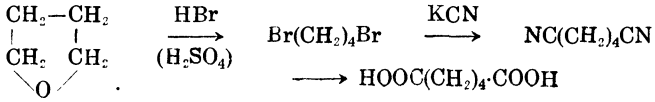
Synthesis of Adiponitrile from Tetrahydrofurane.

By Masaharu KATUNO.

(Received July 29, 1946.)

This paper is the 6th report on the studies of furfural and its related compounds[1].

In the previous reports[2], an attempt was described to prepare butadiene by the catalytic dehydration of tetrahydrofurane, which was obtained from furfural. In the present report an attempt was described to prepare adiponitrile and adipic acid, which have recently obtained an industrial significance as the intermediates for synthetic fibre, from tetrahydrofurane by the following schema:



There are some literatures on the bromination of tetrahydrofurane into tetramethylene dibromide, using HBr in acetic acid[3], fuming hydrobromic acid[4] and dry hydrogen bromide gas[5]. In the present investigation tetrahydrofurane has been brominated with hydrobromic acid in the presence of sulphuric acid, following the method described in "Organic Syntheses". The yield of tetramethylene dibromide was about 64% of the theoretical. The mixture of hydrobromic acid and sulphuric acid was prepared by mixing commercial 45% hydrobromic acid and sulphuric acid or by the reduction of the mixture of bromine and water with sulphurous anhydride, both giving similar results.

There is only an old report on the preparations of adiponitrile from tetramethylene dibromide[6]. Tetramethylene dibromide was heated with aqueous ethanol solution of potassium cyanide and adiponitrile was obtained in the yield of about 75-78%. The reaction of tetramethylene dibromide with aqueous solution of potassium cyanide gives unsatisfactory results, probably due to the low solubility in the aqueous layer. Although the formation of isomers containing isonitril group $CN\cdot(CH_2)_4\cdot$

(1) M. Katuno: *J. Soc. Chem. Ind., Japan*, **46** (1943), 25 B, 180 B, 184 B, 210 B, 214 B.

(2) M. Katuno: ibid., **46** (1943), 210 B, 214 B.

(3) R. Paur: *Bull. Sac. Chem.* (5), **5** (1938), 1053.

(4) Demjanow: *J. Russ. Phys. Chem. Ges.* **24** (1892), 349; Beilsteins Handb. d. Org. Chem. **17** (1933) SIO.

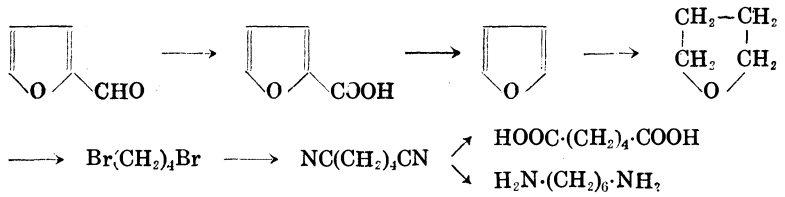
(5) S. Fried & R. D. Kleene: *J. Amer. Chem. Soc.* **62** (1940), 3258; **63** (1941), 2691.

(6) Henry: Zentr, 1901, 11, 807; Beilsteins Handb. d. Org. Chem. Bd. **2** (1920), S 635.

CN and $CN\cdot(CH_2)_4\cdot NC$, in small amounts as byproducts is to be expected, they were not identified in the present investigation.

The hydrolysis of adiponitrile into adipic acid proceeds almost quantitatively by the ordinary method of heating the solution with sulphuric acid.

The hydrogenation of adiponitrile into hexamethylene diamine, on which there are several recent patents and literatures, was not attempted in the present investigation. Although adipic acid and hexamethylene diammine are obtained from phenol, they can also be obtained from furfural by the following rout.



Experimental *1. Tetramethylene dibromide from tetrahydrofurane*: 471 g. of commercial 45% hydrobromic acid (contained 43% of HBr by titration) was mixed with 125 g. of 97% sulphuric acid under cooling. 72 g. (1.0 mol) of tetrahydrofurane (bp. 66.0-67.0°C; $d_4^{20} = 0.8884$; $n_D^{20} = 1.4073$), which was obtained from furfural in the previous reports[7], was mixed with the above acid and heated at about 100°C for about 7 hrs. with reflux condenser under occasional shaking. After cooling, lower layer of tetramethylene dibromide was pipetted out (yield 136 g.). The upper aqueous layer was distilled using 20 cm. Widmer column. Only a negligible amount of tetrahydrofurane fraction was recovered, and from the subsequent fraction boiling between 95°-125°C (125 g.), which separates into two layers, 36 g. of lower layer of tetramethylene dibromide was separated. The yield of tetramethylene dibromide was 172 g. (0.797 mol or 79.7 % of theoretical), and it was redistilled under reduced pressure, and 138 g. of crude tetramethylene dibromide (0.639 mol or 63.9 % of the theoretical) boiling at 90°C/23 mm.-92°C/22mm. was obtained.

Similar results were obtained by using the mixture of hydrobromic acid, water and sulphuric acid which was prepared by the reduction of the mixture of bromine and water with sulphurous anhydride.

The crude tetramethylene dibromide, obtained from three experiments, was purified by redistillation, and a colourless, heavy liquid with stimulative smell was obtained. Bp. = 83°C/18mm.-86°C/19mm. $d_4^{20} = 1.8080$; $n_D^{20} = 1.5175$; $MR_D = 36.21$(found); 36.20(calcd. for $C_4H_8Br_2$). Anal. C:

(7) M. Katuno: *J. Soc. Chem. Ind. Japan*: **46** (1943), 214 B, 210 B.

22.52%, 22.64% ; H: 3.83% ; 3.86% ; Calcd. for $C_4H_8Br_2$: C: 22.25% ; H: 3.73% .

2. *Adiponitrile from tetramethylene dibromide*: **Expt. 1.** A four-necked flask of 500 cc. content, equipped with a mercury-sealed stirrer, dropping funnel, thermometer and reflux condenser, was used. 19 g. of potassium cyanide (0.29 mol) was dissolved in 25 cc. of water, and 56 g. (about 70 cc.) of absolute alcohol was added. 21.6 g. of tetramethylene dibromide (0.10 mol) was dropped under stirring, and the temperature was raised to about 75°C. on the water bath with automatically controlled burner. The mixture was stirred for 4 hrs. at 75°C and then allowed to cool.

Ethanol was removed by distillation up to 90°C using 20 cm. Widmer column. Adiponitrile, which forms the upper layer, was separated, and the aqueous layer was extracted three times with ethyl acetate, and the extract was joined with the adiponitrile layer. The solvent was removed by distillation, and adiponitrile was distilled under reduced pressure. 8.1 g. (0.075 mol or 75% of the theoretical against tetramethylene dibromide) of crude adiponitrile boiling at 140–141°C/6mm. was obtained.

Expt. 2. The amount of ethanol used was decreased, and the separation of adiponitrile was slightly modified. 19 g. (0.29 mol) of potassium cyanide was dissolved in 25cc. of water and 30 cc. of ethanol was added, and heated to 75°C under stirring. 21.6 g. (0.10 mol) of tetramethylene dibromide was dropped in 10 min., and stirred for 5.5 hrs. at 75°C.

After cooling, 50 cc. of water was added to the product to dissolve the crystal separated, and thus adiponitrile formed the upper layer. The mixture was extracted four times with ethyl acetate, and the extract was distilled under ordinary pressure to remove ethyl acetate, and then under reduced pressure. 8.4 g. of crude adiponitrile (0.078 mol ; or 78% of the theoretical) boiling at 173.5–140°C/5 mm. was obtained.

Expt. 3. The reaction was carried out without using ethanol. 21.6 g. (0.10 mol) of tetramethylene dibromide was dropped in the solution of 19 g. of potassium cyanide (0.29 mol) and 25 cc. of water, under stirring at 75°C, and stirring was continued for 6 hrs. Tetramethylene dibromide, which separates as lower layer, was recovered, and the aqueous layer was extracted three times with ethyl acetate, and the extract was joined with the tetramethylene dibromide layer. Ethyl acetate was distilled off, and tetramethylene dibromide was recovered by distillation under reduced pressure. Yield 17.1 g. (79%), boiling between 65–80°C/7.5 mm. Little formation of adiponitrile was observed.

Expt. 4. 95 g. of potassium cyanide (about 1.5 mol) was dissolved in 100 cc. of water and 79 g. (about 100 cc.) of absolute ethanol was added,

and was stirred at 75°C. 108.0 g. (0.50 mol) of tetramethylene dibromide was dropped in about 10 minutes. The temperature of liquid was raised gradually to about 85°C and the boiling of the liquid began. The mixture then was cooled for a while and heated again to 75°C, and was stirred for about 6 hrs.

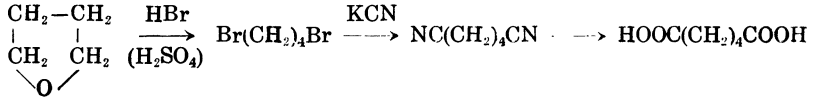
Ethanol was distilled off using 20 cm. Widmer column up to the temperature 90°C. The adiponitrile layer was separated, and the aqueous layer was extracted with ethyl acetate. The solvent was removed by distillation, and 28.8 g. of crude adiponitrile (0.267 mol or 53.4% of the theoretical) boiling between 145–160°C/8 mm. was obtained. Purification of adiponitrile: Crude adiponitrile was redistilled and the main fraction boiling at 165–166°C/16 mm. was obtained. It is a colourless, slightly viscous liquid. $d_4^{20} = 0.9396$; $n_D^{20} = 14390$; $MR_D = 30.91$ (obsd.); 29.54 (calcd. for $(CH_2)_4(CN)_2$). Anal. : C: 66.60%; 66.76%; H: 7.40%; 7.77%; Calcd. for $C_6H_8N_2$: C: 66.64%; H: 7.46%.

3. Adipic acid from adiponitrile: 2.0 g. of adiponitrile was dissolved in 10 g. of 62% sulphuric acid, and heated at about 100°C. The liquid separated crystal after about 2 hrs. After heating more than 3.5 hrs., it was allowed to cool. The crystal of adipic acid was washed with a small amount of water, wiped with filter paper, and dried to constant weight by steam oven and evacuated desiccator. 2.7 g. (100% of the theoretical) of crude adipic acid was obtained. It was recrystallised twice from water after treating with charcoal, and 1.1 g. (41% of the theoretical) of pure adipic acid was obtained. It is a snowwhite crystal with mp. 149.0–149.5°/C (uncorr.).

Anal. C: 49.14%; 48.95%; H: 6.84%; 6.94%. Calcd. for $C_6H_{10}O_4$: C: 49.31%; H: 6.90%.

Summary.

The synthesis of adiponitrile and adipic acid from tetrahydrofurane, which was obtained from furfural, has been attempted, according to the following schema:



In conclusion, the author wishes to express his thanks to Mr. Y. Ban and Mr. M. Kurokawa for their guidance, to Mr. Hirosi Andoo for the assistance in a part of experiment and to the Research Section of the Takeda Chemicals Co. for the microelementary analysis.

Imperial Fuel Research Institute;
Kawaguti Saitama.

Hydrogenation of Furfural and Furfuryl Alcohol. IV.

Hydrogenation of Furfural into Furfaryl (Tetrahydrofurfuryl) Alcohol by the Combination of Copper Chromium Oxide Catalyst and Nickel Kieselguhr Catalyst.

By Masaharu KATUNO.

(Received July 29, 1946.)

This paper is the 7th report on the studies of furfural and its related compounds[1]. In a previous report[2], it was observed that the hydrogenation of furfural using nickel kieselguhr catalyst yields furfaryl alcohol or tetrahydrofurfuryl alcohol (about 60~75% of the theoretical yield), together with lower and higher boiling byproducts. On the other hand, the hydrogenation of furfural into furfuryl alcohol using copper chromium oxide catalyst[3], and the hydrogenation of furfuryl alcohol into furfaryl alcohol using nickel kieselguhr catalyst[4], proceed smoothly and furfaryl alcohol was obtained with little byproducts. It was suggested that for the production of furfaryl alcohol it seemed advantageous to carry out the hydrogenation in two steps, namely furfural into furfuryl alcohol using copper chromium oxide, and then furfuryl alcohol into furfaryl alcohol using nickel kieselguhr catalyst.

In this paper some investigations are reported on the hydrogenation of furfural into furfaryl alcohol by using both copper chromium oxide catalyst and nickel kieselguhr catalyst.

Furfural (1 mol) was hydrogenated into furfuryl alcohol by using copper chromium oxide catalyst at about 140°C, absorbing about 1 mol of hydrogen. This reaction product was then hydrogenated by adding nickel kieselguhr catalyst, without separation and purification of furfuryl alcohol. About 2 mol hydrogen was absorbed rapidly at about 120°C, and then furfaryl alcohol (yield about 83–84% of the theoretical), was obtained with little byproducts (see experiments P 51 and P 68 in the Table 1).

In the previous report it was observed and concluded that furfural was intrinsically more inert than furfuryl alchol against the hydrogention over nickel kieseluhr catalyst, but it was not due to the presence of a small amount of catalyst poison, like thiophene in benzene. The present experimental results that the hydrogenation of the second step proceeds

(1) M. Katuno: *Soc. Chem. Ind., Japan*, **46** (1943), 25 B, 180 B, 184 B, 210 B, 214 B.
(2) M. Katuno: ibid., **46** (1943), 25 B.
(3) M. Katuno: ibid., **46** (1943), 180 B.
(4) M. Katuno: ibid., **46** (1943), 184 B.

rapidly, also confirm that furfural does not contain catalyst posion, such as sulphur compounds.

Furfural (1 mol) was then hydrogenated at about 140°C, by using copper chromium oxide catalyst and nickel kieselguhr catalyst together, which were prepared separately before use by thermal decomposition of Cu(OH) (NH_4) (CrO_4) and by reduction of $NiCO_3$-kieselguhr. About 3 mol of hydrogen were absorbed, and furfaryl alchol (about 74–79% of theoretical yield) was separated from the product. The yield was slightly lower than in the above-mentioned method, and small amounts of byporducts were observed (P 52 and P 61). In this hydrogenation, it is probable that furfural is partly hydrogenated in two steps, first into furfuryl alcohol by copper chromium oxide catalyst, and then into furfaryl alcohol by nickel catalyst, in good theoretical yield, and partly hydrogenated directly into furfaryl alcohol by the nickel catalyst with considerable amounts of lower and higher boiling byproducts, as observed in the preuious reports[5]. The yields are, therefore, a little lower than in the above two step hydrogenation.

In the above experiments, copper chromium oxide catalyst and nickel kieselguhr catalyst were prepared separately before use from Cu (OH) (NH_4) (CrO_4) and Nickelcarbonate-kieselguhr, respectiveiy. Mixed catalysts of Cu (OH) (NH_4) (CrO_4) and $NiCO_3$-kieselguhr were then employed for the hydrogenation of furfural. Both catalysts were mixed mechanically by grinding in a mortar in the ratio of 1 : 1 or 1 : 2 by weight, or mixed in the state of precipitates as described in the experimental details.

Furfural (1 mol) was hydrogenated at about 140°C by using the mechanically mixed catalyst, which was reduced at about 250°C, before use (Expt. P 53). About 1 mol of hydrogen was absorbed rapidly and then hydrogenation became slow, and about 1.33 mol of hydrogen was absorbed in about $4\frac{25}{60}$hrs. The absorption of hydrogen is also slow by the rise of the temperature to about 160°C after hydrogenation at about 140°C (Fxpt. P 107). These results show that nickel is not reduced inductively by copper, probably because of the unintimate contact between nickel and copper. By the reduction at about 400°C after reduction at about 250°C, the catalyst can hydrogenate furfural into furfaryl alcohol in about 70% theoretical yield, absorbing about 3 mols of hydrogen, owing to the reduction of nickel (Expt. P 62).

The mixed catalyst in the state of precipitation, after reducing at about 250°C, can hydrogenate furfural into furfayl alcohol, absorbing about 3 mols of hydrogen, owing to the induced reduction of nickel (Expt. P 72). The catalyst, after thermal decomposition at about 250°C without reduction, cannot hydrogenate furfural into furfaryl alcohol,

(5) M. Katuno: *J. Soc. Chem. Ind., Japan,* **46** (1943), 25 B.

the hydrogenation becoming slow after rapid absorbtion of about 1 mol of hydrogen, and about 1.26 mol of hydrogen was absorbed in about $5\frac{15}{60}$hrs. (Expt. P 106′).

These results using mixed catalysts are inferior to the above results using two catalysts prepared separately before use.

Experimental Details. *1. Catalysts: Copper chromium oxide catalyst:* It was prepared as described in the previous report[6], following the description of Edgar and Calingaert[7] with slight modification. Namely, brown precipitate Cu $(OH)(NH_4)(CrO_4)$ was prepared from copper nitrate and ammonium bichromate solution with ammonia water, washed with water, filtered, dried in a steam oven and powdered and stored in a desiccator. It was decomposed into $2CuO + Cr_2O_3$ by heating at about 250°C for one hour.

I : I (by weight)-nickel-kieselguhr catalyst: It was prepared as described in the previous report[8]. Nickl carbonate was precipitated on kieselguhr in the ratio Ni : kieselguhr = I : I (by weight), from Nickel nitrate solution with sodium carbonate and a small amount of sodium hydroxide. The precipitate was washed, filtered, dried in a steam oven, powdered and stored in a desiccator. It was reduced at about 450°C in a stream of hydrogen for one hour before use. *Mechanically mixed catalyst of copper chromium oxide and nickel kieselguhr catalyst*: $Cu(OH)(NH_4)(CrO_4)$ and nickelcarbonate-kieselguhr were mixed in the ratio of I : I and I : 2 by weight by grinding in a mortar. For the reduction of the catalyst, it was heated to about 250°C in a stream of carbon dioxide gas and then hydrogen was introduced very slowly at first and finally rapidly[9], in order to prevent the temperature rise of the catalyst.

Mixed catalyst of copper chromium oxide and nickel kieselguhr in the state of precipitates: $Cu(OH)(NH_4)(CrO_4)$ was precipitated from calculated amounts of copper nitrate solution (content of copper was analysed) and (ammonium bichromate with ammonia water, which was neutralised with nitric acid solution when added in excess, in order to preciptitate copper as completely as possible. The precipitate of Cu $(OH)(NH_4)(CrO_4)$ was washed by decantation. On the other hand, a calculated amount of nickel carbonate was precipitated on kieselguhr (nickel : kieselgur = I : I by weight) from calculated amount of nickel nitrate solution (content of Ni was analysed) with sodium carbonate and a small amount of sodium hydroxide solution, and the precipitate was

(6) M. Katuno: *J. Soc. Chem. Ind., Japan,* **46** (1943), 180 B.
(7) G. Edgar & G. Calingaert: *Ind., Eng. Chem.* **26** (1934), 878.
(8) M. Katuno: *J. Soc. Chem. Ind., Japan,* **46** (1943), 25 B.
(9) M. Katuno: *J. Soc. Chem. Ind., Japan,* **45** (1942), 390 B.

washed. The two precipitates were then mixed together intimately, filtered, dried, powdered and stored in a desiccator. The amount of copper and nickel were calculated for $Cu(OH)(NH_4)(CrO_4)$: nickelcarbonate-kieselguhr = I : I by weight. The reduction of the catalyst was carried out as described before.

2. Hydrogenation: A horizontal shaking autoclave of about 660 cc. content was used. The hydrogenation was carried out with the initial pressure of about 88–102 atm; (at room temperature). Hydrogen was charged from bomb when the pressure dropped below 50 atm. Hydrogenation was continued in the most cases till the pressure became constant after complete hydrogenation. Furfural used was redistilled under reduced pressure and had yellow or light brown color.

3. Fractionation of the products: The procedure is the same as that in the previous paper[10]. The product was pipetted out into 300 cc. modified Claisen flask[11] or three necked flask[11], and weighed. The product was fractionated using 20 cm. Widmer column, first under atmospheric pressure, and the fraction boiling up to 90°C was separated (Fraction A), which consists mainly of the aqueous azeotropic mixture of methyltetrahydrofuran, etc. in the case of the hydrogenation using nickel catalyst. The pressure was then reduced to about 50–90 mm., and the fraction boiling up to 80–90°C was collected (Fraction B). This fraction consists of a considerable amount of water, and probably, the aqueous azeotropic mixture of n-amyl alcohol mainly.

The pressure was then reduced to about 20 mm., and the fraction boiling up to 90°C was collected (Fraction C). This fraction boils constantly at about 80°C under 20 mm., and consists mainly of furfaryl alcohol in the case of nickel catalyst, and mainly of furfuryl alcohol in the case of incomplete hydrogenation (Expt. P 53, P 106, P 107). In some cases the liquid in the flask was distilled at the temperature below 90°C. The fraction C was regarded as crude furfaryl alcohol or, in a few cases (P 53, P 106, P 107), as furfuryl alcohol.

The distillation was further continued till the decomposition took place, and the distillate (fraction D) probably consists of pentanediols. The residue (fraction E) consists of the catalyst and the more highboiling viscous substance.

Summary.

1. Furfural was hydrogenated into furfuryl alcohol by using copper chromium oxide catalyst under high pressure. Then the product was

(10) M. Katuno: *J. Soc. Chem. Ind., Japan,* **46** (1943), 25 B.
(11) M. Katuno: *J. Soc. Chem. Ind., Japan,* **46** (1943), 209 B.

further hydrogenated by adding nickel kieselguhr catalyst, without separation and purification of furfuryl alcohol. The hydrogenation proceeded rapidly and furfaryl alcohol about 83–84% of the theoretical yield was obtained.

2. Furfural was hydrgenated by using copper chromium oxide catalyst and nickel kieselguhr catalyst, which were prepared separately before use. The hydrogenation proceeded rapidly, and furfaryl alcohol, (about 74~79% of the theoretical yield) was obtained, which is slightly lower than in the above procedure.

3. The mixture of $Cu(OH)(NH_4)(CrO_4)$ and nickelcarbonate kieselguhr, mixed mechanically or in the state of precipitates, was used for the hydrogenation of furfural, after reducing it with hydrogen or after thermal decomposition without reduction. The results was less satisfactory compared with the above two procedures.

The author wishes to express his thanks to Mr. Y. Ban and Mr. M. Kurokawa for their guidance, and to Mr. S. Nagaoka for his assistance in experimehts.

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Table 1. Hydrogenation of furfural (96 g. or 1.0 mol of furfural was used.)

Exptl. No.	Catalyst	Amount of Cu or Ni (g)	Hydrogenation: Temp. (°C)	Time (hrs)	Pressure drop (atm) (0°C)	Absorption of H_2[1] (mol)	Fractionation of the product: Fract. A (g)	Fract. B (g)	Fract. C (crude furfaryl alcohol) Yield (g)	Yield (mol)	Theor. yield (%)	Fract. D (g)	Residue (g)	References
P 51	$2CuO+Cr_2O_3$	1.2	(137~146°) 140	$3\frac{25}{60}$	43.1	1.07								
	followed by 1:1-Ni-kieselguhr	2.6	(117~121°) 120	$2\frac{55}{60}$	78.6	1.93	~90° 0	65°/82~80°/82 1.1	77°/21~90°/22 85.2	0.835	83.5	0	15.0	
					Total 122.2	3.00								
P 68	$2CuO+Cr_2O_3$	1.2	(138~143°) 140	4.0	42.7	1.05								
	followed by 1:1-Ni-kieselguhr	1.3	(116~121°) 120	$2\frac{40}{60}$	84.2	2.06	~90° 0	48°/83~93°/83 1.4	79.5°/22~90°/26 85.0	0.832	83.2	0	8.3	
					Total 126.9	3.11								
P 52	$2CuO+Cr_2O_3$ 1:1-Ni-kieselguhr (Prepared separately and used together.)	1.2 } 2.6 }	(136~143°) 140	$3\frac{55}{60}$	125.9	3.08	67~90° 0.5	55°/86~93°/86 0.8	86°/24~95°/22 80.3	0.787	78.7	—	20.7	
P 61	$2CuO+Cr_2O_3$ 1:1-Ni-kieselguhr (Prepared separately and used together.)	1.2 } 1.3 }	(136~144°) 140	$3\frac{50}{60}$	129.7	3.18	~90° 0	57°/74~90°/74 0.2	78°/18~100°/20 75.9	0.743	74.3	100°/20~106°/10 2.4	19.1	
P 106′	$2CuO+Cr_2O_3$	1.2 }	(138~141°) 140	3.0	45.8	1.12								
			(159~165°) *interval*	$\frac{20}{60}$	0.0	0.00								
	1:1-Ni-kieselguhr	1.3 }	then 160	$1\frac{55}{60}$	5.5	0.14	—	59°/52~85°/52 5.9	77°/18~95°/18 (52.7)[3]	(0.538)[3]	(53.8)[3]	95°/18~125°/18 5.4	31.5	Resinification took place a little.
	(Mixed catalyst[2] by precipitation was heated at 250° for 1 hr.)				Total 51.3	1.26								
P 53	$2CuO+Cr_2O_3$ 1:1-Ni-kieselguhr (Mechanically mixed catalyst[2] was reduced at 250° for 1 hr.)	1.2 } 2.6 }	(137~145°) 140	$4\frac{25}{60}$	54.0	1.33	70~90° 0.6	47°/76~72°/76 1.0	80°/21~85°/27 (85.5)[3]	(0.872)[3]	(87.2)[3]	0	14.5	
P 107	$2CuO+Cr_2O_3$	1.2 }	(140~145°) 140	$1\frac{15}{60}$	46.3	1.14								
			(156~163°) *interval*	$\frac{20}{60}$	−0.8	−0.02								
	1:1-Ni-kieselguhr	1.3 }	then 160	$2\frac{35}{60}$	11.1	0.27	—	38°/60~60°/55 4.3	79°/20~93°/22 (62.5)[2]	(0.637)[3]	(63.7)[3]	93°/22~123°/25 several cc.	28.0	Resinification took place a little.
	(Mechanically mixed catalyst[2] was reduced at 250° for 1 hr.)				Total 56.6	1.39								
P 62	$2CuO+Cr_2O_3$	1.2 }	(136~142°) 140	$3\frac{5}{60}$	93.6	2.30								
			(159~161°) *interval*	$\frac{25}{60}$	11.9	0.29								
	1:1-Ni-kieselguhr	1.3 }	then 160	$1\frac{50}{60}$	15.9	0.39	~90° 0	47°/82~100°/82 2.4	76°/22~102°/22 71.2	0.698	69.8	102°/22~109°/23 3.7	22.6	
	(Mecnically mixed catalyst[2] was reduced at 250° then at 400° each for 1 hr.)				Total 121.4	2.98								
P 72	$2CuO+Cr_2O_3$	1.2 }	(135~146°) 140	$2\frac{10}{60}$	50.5	1.24								
			(155~161°) *interval*	$\frac{15}{60}$	2.4	0.06								
	1:1-Ni-kieselguhr	1.3 }	then 160	$3\frac{40}{60}+2\frac{30}{60}$	74.9	1.84	71~93° 1.9	47°/85~100°/85 0.4	80°/21~92°/22 67.7	0.663	66.3	92°/22~124°/22 2.6	27.6	
	(Mixed catalyst[2] by precipitation was reduced at 250° for 1 hr.)				Total 127.8	3.14								

(1) Calculated assuming the volume of gas in the autoclave to be about 550 cc., and the gas to be a perfect gas.

(2) Mixture of $Cu(OH)(NH_4)(CrO_4)$ and Nickelcarbonate-kieselguhr (Nickel:kieselguhr≒1:1). (3) Regarded and calculated as crude furfuryl alcohol.

Malhelpa Afiniteco de Benzedrino-Derivaĵoj al Amino-oksidazo.*

De Jukito ÔTA.

(Ricevita la 12-an de Novembro, 1946.)

Kiam benzedrino (V) estas en la medio, la oksidado de tiramino (S) per amino-oksidazo (E) marŝas jene:

$$S+E \rightleftarrows SE \rightarrow \text{produkto}+E$$

$$V+E \rightleftarrows VE\,.$$

La afiniteco de V al E devas esti en inversa proporcio de l'disocio-konstanto (K) de l'kombinaĵo VE, kaj tiun ĉi ni provas kalkuli per la formulo:

$$1-\frac{v'}{v} = \frac{[V]}{E\left(1+\frac{[S]}{K_m}\right)+[V]}$$

Kie signifas; v: rapideco de l'oksidado sen-ekziste de benzedrino,
v': rapideco de l'oksidado malhelpata de benzedrino, kaj
K_m: Michaelis-konstanto ($10^{-3\,6}$ mol/litro sub mia esplorkondiĉo[2]).

Studinte per helpo de manometro v kaj v' respektive, mi kalkulis valorojn de K de benzedrino-derivaĵaroj.[3] Ĉefaj rezultatoj estas kiel jene:

	Benzedrino-derivaĵoj	$-\log K$
1.	dl 1-fenilo 2-amino propano (benzedrino)	4.6
2.	d 1-fenilo 2-amino propano	4.6
3.	d 1-fenilo 2-metilamino propano (filopono)	4.2
4.	d 1-fenilo 2-dimetilamino propano	4.2
5.	d 1-fenilo 2-metil, etilfenilamino propano	3.4
6.	dl 1-fenilo, amino butano	—*
7.	dl 1-fenilo 2-amino butano	3.9
8.	dl 1-fenilo 3-amino butano	4.5
9.	dl 1-fenilo 5-amino heksano	4.3
10.	dl 1-fenilo, hidroksilo 2-amino propano	3.1
11.	dl 1-fenilo, hidroksilo 2-metilamino propano (efedrino)	3.0

(1) Komparu al Mann kaj Quastel; *Biochem. J.*, **34** (1940), 414.

(2) pH 7.6, 30°, tiramina oksidado per oksigeno katalize de dializita hepato-ekstrakto.

(3) Estis ekzamitaj ĉirkaŭ kvardek kemiaĵoj bonvole donacitaj respektive de Nagai Kemia Laboratorio (D-ro W. Nagai) kaj de Farmakologia Instituto (P-ro D-ro A. Ogata) de Tokio Imperia Universitato.

12.	dl 1-fenilo, etoksilo 2-metilamino propano	3.3
13.	dl 1-fenilo, hidroksilo 2-dimetilamino propano	2.9
14.	dl 1-3:4 metilendihidroksilfenilo 2-amino propano	4.7
15.	dl 1-3:4 metilendihidroksilfenilo, metoksilo 2-amino propano	3.1
16.	dl difeniloj, amino metano	—**
17.	dl 1,3-fenilo 2-amino propano	—**
18.	dl fenilo, etilfenilo, amino metano	—**
19.	dl fenilo, cikloheksilo, amino metano	—**
20.	dl 1-difeniloj z-amino etano	—**

* Rilate detalojn de l'esplormetodo k.a., vidu J. Ôta; *J. Jap. Chem. Soc.* (en jap. lingvo), nepublikigita.

** Ne povis malhelpi la agon de l'amino-oksidazo, nome, ne havas afinitecon al la enzimo.

El la tabelo ni povas elpreni sekvantajn regulajn paralelecojn de kemiaj konstituoj de benzedrino-derivaĵoj (ϕ–CH_2–····–$CH(NH_2)$–····–CH_3) al la afinitecoj de l'derivaĵoj al la amino-oksidazo:

1. Ju pli proksime la amino.grupo troviĝas de ia fina metilo-grupo de l'hidrokarbono-ĉeno, des pli granda la afiniteco.

2. Koncerne al la longeco de l'hidrokarbono-ĉeno, la ĉeno el tri karbono-atomoj portas la plej granda afiniteco. Ju pli longa (kaj eble ankaŭ ju pli mallonga,[4] ol tri karbonoj la ĉeno, das pli malgrauda la afiniteco.

3. Enmeto de alkilo-, alkileno- (aŭ fenilo-grupoj) en la amino grupo rezultas redukton de l'afiniteco.

4. Enmete de brancо de hidroksilo aŭ alkoksilo en la hidrokarbono-ĉeno ankaŭ rezultas redukton de l'afiniteco.

5. Enmeto de hidroksilo aŭ ĝia derivaĵo en la fenilo estas favora por la afiniteco.

6. Se la finaĵoj de l'hidrokarbono-ĉeno estas ambaŭ fermantaj de feniloj (aŭ ĝiaj derivaĵoj) aŭ de fenilo kaj ciklo-heksilo, afiniteco malaperas.

7. Nenian preferecon al la optikaj isomeroj (almenaŭ de benzedrino) ŝajnas havi la oksidazo.

Estas notinde, ke preskaŭ tute samaj regulecoj al la supre skribitaj, escepte de la artikolo 1., estas trovataj ankaŭ en substrato-aminoj. Ĉu ia alkilamino servas al la amino-oksidazo kiel enzimo-substrato aŭ kiel enzimo-veneno, dependas sole de l'loko de ĝia amino-grupo sur la hidrokarbono-ĉeno! Alkilamino, kiu havas la amino-grupon al la finaĵo de l'hidrokarbono-ĉeno, estas oksidebla per lo oksidazo,[5] dum tiu, kiu havas la amino-grupon sur la mezo de l'ĉeno, malhelpas la oksidadon!

Mi dankas al P-ro D-ro H. Tamiya (Tokio Imp. Univ.) kaj P-ro D-ro

(4) Analoge konsidere la fakton, konita pri substrato-amino, ke metilo aŭ etilamino ne aŭ preskaŭ ne estas oksidebla per la oksidazo. Komparu al Blaschko, Richter kaj Schlossmann: Biochem. J., **31** (1937), 2187.

(5) Komparu al Blaschko k a., supre citita.

F. Egami (Nagoya Imp. Univ.) por iliaj bonkoraj instruadoj. Tiu ĉi studo estis helpata de l'Subvencio al Scienca Esplorado el Ministrejo de Edukado.

Summary.

(1) The competitive inhibitation of benzedrine and similar compounds upon amine oxidase was manometrically studied.

(2) The relation between the inhibiting action and the constitution of these amines was discussed.

P.S. Laŭ Mann kaj Quastel[1] la bone konata stimulanta ago de benzedrino k.s. sur la centronervo-sistemo eble originas de ilia inhibiteca efekto al la amino-oksidazo. Mi volas trakti en alia okazo la problemon, ĉu la nun gajnitaj valoroj de K de benzedrino-derivaĵoj povas indiki la grandecon de ilia farmakolgiaj efektoj. (J. Ô.)

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