UDC 615.778.47[547.292]-011

145. **Setsuo Kiryu and Sadao Iguchi** : Studies on Pyrone Derivatives. XI.[*1] Dimorphism of Dehydroacetic Acid.

(*Institute of Pharmaceutical Sciences, Faculty of Medicine, Kyushu University*[*2])

Studies on dehydroacetic acid have been made from various aspects by many investigators, but papers reporting the solid state or crystal form of this compound cannot be found in the past literature except one, which suggested the existence of polymorphism through microscopic observation.[1)]

Recently, it was recognized definitely that dehydroacetic acid had two kinds of crystal form. Microscopic observations showed that the crystals (α-form) of dehydroacetic acid recrystallized from usual organic solvents, *i.e.* ethanol or benzene, changed into fine polycrystalline form when heated at 80~90° (Plate 1). Study on this phenomenon through differential thermal analysis revealed that the crystals of α-form showed heat absorption at 80° (Fig. 1a).

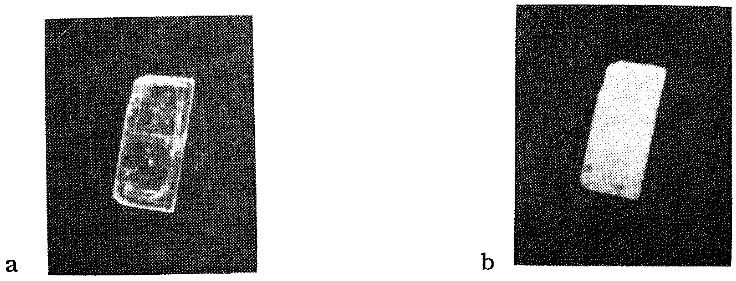

Plate 1. Transition Process of Dehydroacetic Acid Crystal : (a) At room temperature, (b) At 90°

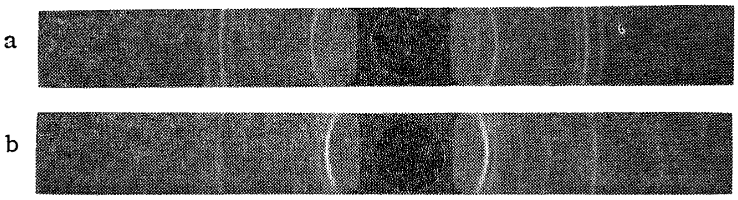

Plate 2. X-Ray Powder Photographs of Dehydroacetic Acid
(a) α-Form (b) β-Form

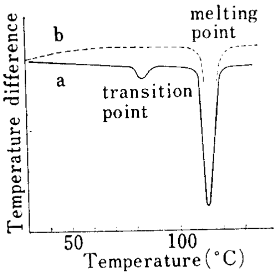

Fig. 1. Thermograms of Dehydroacetic Acid
(a) α-Form
(b) β-Form

On the other hand, such changes by heating could not be observed microscopically with crystals (β-form) obtained by cooling the melted dehydroacetic acid, and thermogram of these crystals had no peak of heat absorption except that of melting (Fig. 1b).

[*1] Part XI : This Bulletin, **11**, 390 (1163).

[*2] Katakasu, Fukuoka (吉柳節夫, 井口定男).

1) A. Kofler : Mikrochemie, **34**, 15 (1948).

In spite of these differences, the two kinds of crystals showed no depression in the melting point on admixture (m.p. 110°), and showed identity in their elemental analyses and ultraviolet spectra (λ_{max} 306 mμ, log ε 4.125 in acid solutions).

Besides these, it was also observed that crystals of β-form returned again to those of α-form when recrystallized from organic solvents like benzene. From these facts, it was naturally deduced that crystals of these two kinds of dehydroacetic acid were the same in their molecules but might be different in their crystal structures. The result of comparative examination by X-ray powder method gave a definite conclusion that they were quite different in their crystal structure. After heating of α-form crystals above 80° for a while, X-ray diffraction pattern of the crystals was that of β-form (Plate 2).

It was therefore shown that dehydroacetic acid occurred in two kinds of crystals, one of which was α-form (monoclinic), stable at a low temperature, and the other was β-form (triclinic), stable at a high temperature, and that the transition from α- to β-form occurred at 80°.

In order to obtain some crystallographical data, oscillation, and all zero level and some first level Weissenberg photographs of both forms about three principal axes were taken, using Cu Kα radiation.

Probably because of large temperature factor, few high angle reflections necessary for precise cell constants determination were recorded, therefore the constants were only roughly estimated from rather lower reflections ($\theta < 60°$) in Weissenberg films in this case.

The space group of $P2_1/c$ was considered to be reasonable for α-form since, in the reflection data, no regular absence was observed except for $(0k0)$ when k was odd and $(h0l)$ when l was odd.

Crystal data of both forms are listed in Table I.

Table I. Crystal Data of Dehydroacetic Acid

	α-Form	β-Form
Crystal system	monoclinic	triclinic
Lattice constants	a 18.2 Å	a 10.2 Å
	b 11.5 Å	b 11.7 Å
	c 7.45 Å	c 14.7 Å
		α 112°
	β 92°	β 102°
		γ 89°
Cell volume	1.56×10^3 Å^3	1.58×10^3 Å^3
Observed density[a]	1.44 g./cm^3	1.44 g./cm^3
Calculated density	1.43 g./cm^3	1.41 g./cm^3
Number of molecules in a unit cell	8	8
Space group	$P2_1/c$	$P1$ or $P\bar{1}$

a) Floatation method (hexane-CCl_4)

Experimental

Preparation of Crystals——Crystals of α-form were generally obtained by recrystallization from usual organic solvents, EtOH, benzene, etc. m.p. 110°. *Anal.* Calcd. for $C_8H_8O_4$: C, 57.22; H, 4.76. Found : C, 57.79; H, 4.98. Crystals of β-form was prepared by heat treatment of the α-form crystals at above 80°. m.p. 110°. *Anal.* Found : C, 58.02; H, 4.78.

Single crystals of α-form for X-ray measurements were obtained by slow evaporation of benzene solution at room temperature, and those of β-form by slow cooling of dehydroacetic acid from its melting state.

Differential Thermal Analysis——Instrument : Shimadzu DT-10 type. Inert material : α-Al_2O_3. Heating rate : 2°/min.

X-ray Measurement——Powder method : Cr Kα radiation using V filter. Camera diameter 9.00 cm. Weissenberg method : Cu Kα radiation using Ni filter. Camera diameter 5.73 cm.

The authors wish to thank Prof. T. Okada and Dr. A. Okazaki, Department of Physics of this University, for their kind guidance and help in X-ray measurements. The authors also wish to express their gratitudes to Prof. T. Oyama, Department of Applied Science of this University, for his kind advice and help in differential thermal analysis.

This work was partly supported by the Grant-in-aid for Scientific Research provided by Ministry of Education, to which they are also grateful.

Summary

It was definitely found that dehydroacetic acid had two kinds of crystals, one of which was α-form (monoclinic), stable at a low temperature, and the other was β-form (triclinic), stable at a high temperature. Transition from α-form to β-form occurred at 80°. Lattice constants and other crystal data of these two kinds of crystals were reported.

(Received August 27, 1962)

UDC 547.859.3.07

146. **Yasuo Makisumi**: Studies on Azaindolizine Compounds. XIV.[*2] Transetherification in *s*-Triazolo[1,5-*a*]pyrimidines.

(*Shionogi Research Laboratory, Shionogi & Co., Ltd.*[*1])

Oliverio[1] reported that *o*- or *p*-nitrophenyl methyl ether was transformed into *o*- or *p*-nitrophenethol by heating with ethanol in the presence of alkali and this reaction was reversible. The same reaction on 2,4-dinitrophenyl ethers was reported by Ogata and Okano.[2] Recently, such transetherification reaction was reported on the aromatic heterocyclic compounds *e.g.* benzothiazole,[3,4] benzodiazine,[5] and pyrimidine[6] fields. From the results of these papers, the transetherification reaction is considered to be the nucleophilic substitution by the alcoholate anions and also to be able to occur at the only position possessing high nucleophilic reactivity.

In the previous paper,[7] the author reported that 5- and 7-positions of the *s*-triazolo[1,5-*a*]pyrimidine ring were very reactive towards the nucleophilc substitution and the 7-position was more reactive than the 5-position. In connection with these facts, the transetherification of the alkoxyl groups at the 5- and 7-positions in *s*-triazolo[1,5-*a*]pyrimidines was investigated.

In the previous work,[8] 5-methyl-7-alkoxy-*s*-triazolo[1,5-*a*]pyrimidines (Ia and Ib) were synthesized by the reaction of the corresponding 5-methyl-7-chloro derivative (I) with an equimolar amount of sodium alkoxide at room temperature. By the same method,

---

[*1] Fukushima-ku, Osaka (牧角徳夫).

[*2] Y. Makisumi: This Bulletin, **11**, 129 (1963).

[1] A. Oliverio: Atti X° congr. intern. chim., **3**, 258 (1939). (C. A., **33**, 9302 (1939)).

[2] Y. Ogata, M. Okano: J. Am. Chem. Soc., **71**. 3211 (1949).

[3] H.H. Fox, M.T. Bogert: *Ibid.*, **63**, 2996 (1941).

[4] Y. Mizuno, K. Adachi: Yakugaku Zasshi, **72**, 269 (1952).

[5] K. Adachi: *Ibid.*, **75**, 1426 (1955).

[6] M. Watatani: Ann. Rept. Takamine Lab., **12**, 37 (1960).

[7] Y. Makisumi: *Ibid*, **9**, 801 (1961).

[8] Y. Makisumi, H. Kano: *Ibid.*, **11**, 67 (1963).