The heat of fusion was reported as 7.9 ± 0.5 kcal. mole^{-1} with a heat of sublimation of 96.6 ± 0.5 kcal. mole.$^{-1}$ Inasmuch as the deviation from linearity may alternatively be accounted for by assuming a reasonable ΔC_p for the sublimation process and as the reported melting points are rather lower than would be expected from comparison with other fluorides,[3] we have undertaken a determination of the plutonium trifluoride melting point in the apparatus shown in Fig. 1. An inconclusive attempt to determine the melting point of 60 micrograms of plutonium trifluoride on a tantalum filament in purified argon yielding successive values of 1435, 1560 and 1635° has been reported by Robinson.[4] X-Ray diffraction examination indicated the formation of plutonium oxyfluoride (PuOF) in the sample. For the present work about 350 mg. of plutonium trifluoride was prepared by hydrofluorination in a platinum reactor[5] of uranium-free, spectroscopically pure plutonium dioxide. X-Ray diffraction examination and spectrochemical analyses after the measurements confirmed the purity and crystalline phase of the plutonium trifluoride and the absence of corrosion of the tantalum. The trifluoride was pelleted into an annular cylinder, placed in the tantalum crucible and a previously outgassed beryllia microfurnace. The microfurnace assembly was then placed within a bulb attached to a high vacuum apparatus. After outgassing the system, the transition temperature was then located by thermal analysis.

Continuous potential curves of the platinum *versus* platinum plus 10% rhodium thermocouple were automatically traced on a Leeds and Northrup Speedomax recorder checked against a Rubicon Type B potentiometer. These curves were essentially interpolations over ten to thirty degree ranges, the limits of which were established by direct optical pyrometer observation of the tantalum crucible at temperature equilibrium. Since essentially "black body" conditions obtain for the tantalum crucible, no emissivity correction is involved. Both optical pyrometers were calibrated against a standard lamp and also against the melting point of palladium in the present apparatus upon substitution of a beryllia liner. Direct observation of the fusion and solidification points with the optical pyrometer were found to agree with the thermocouple values and with each other regardless of the sign or magnitude of the thermal head. Corrections were applied for the transmissivity of the Pyrex window and after many transitions a compensation amounting to several degrees was required to correct for the sublimed film of plutonium trifluoride on the window. Repeated transitions were observed under various thermal heads both in high vacuum and under 10^{-2} atm. of argon, fusion temperature (11 observations): 1426 ± 2°; solidification temperature (13 observations): 1425 ± 3° the uncertainties indicated are average deviations. The plutonium trifluoride had fused, and no thermal effect was detected near the temperature previously interpreted as the melting point.[1] We believe that a phase transition with a molar enthalpy change greater than two kilocalories would have been apparent.

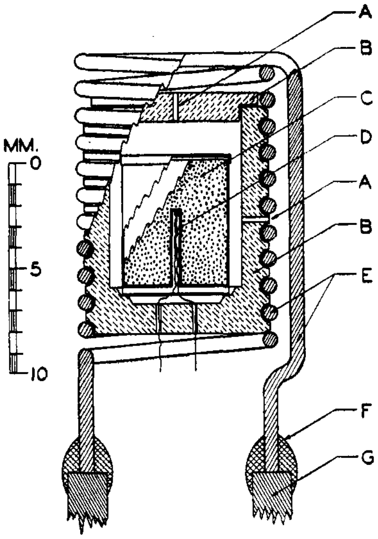

Fig. 1.—PuF_3 melting point apparatus: (A) optical pyrometric sighting ports, (B) beryllia furnace block and cover, (C) PuF_3 pellet in a covered tantalum crucible with entrant thermocouple well, (D) thermocouple, (E) 0.6 mm. diam. tungsten wire heating coil, (F) platinum weld, (G) 2 mm. diam. tungsten electrodes.

By use of the Gaussian criterion for closeness of fit, a three constant equation fitted by weighted least squares indicated as good agreement with the vapor pressure data reported by Phipps, *et al.*,[2] as did their two similarly fitted linear equations previously reported.

The ΔC_p of sublimation corresponding to this equation was −32 cal. mole^{-1} deg.$^{-1}$. A least squares treatment with an assumed value of ΔC_p = −15 cal. mole^{-1} deg.$^{-1}$ and two arbitrary constants also fits the data well and yielded the equation

$$\log_{10} P_{\text{mm}} = -24{,}917T^{-1} - 7.5513 \log T + 38.920$$

valid from 1200 to 1660°K. for the dissociation pressure and a value of 89 kcal. mole^{-1} for the heat of sublimation of 1400°.

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The Condensation of Ethyl Acetoacetate to Isodehydroacetic Acid and Ethyl Ester

By Richard H. Wiley and Newton R. Smith[1]

The sulfuric acid catalyzed condensation of ethyl acetoacetate to a mixture of isodehydroacetic acid

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(1) The authors are indebted to the Research Corporation for a grant in support of this research.

and its ethyl ester has been known for many years.[2,3] The work of Goss, Ingold and Thorpe[4] has shown that the ester can be obtained as the major product of the reaction when dry hydrogen chloride is used as the condensing agent. As part of a study to determine the possibility of obtaining the acid as the major product, we have undertaken an investigation of the effect of varying reaction conditions on the course of the condensation. The data obtained, along with additional information on the hydrolysis of ethyl isodehydroacetate to the acid and on esterification of the acid, has established some facts about the course of the reaction and the structure of these compounds which we wish to report in this paper.

The condensation takes place at room temperature when acetoacetic ester is dissolved in a large volume of sulfuric acid. In this study the effect of the concentration of reactants, temperature, time of the reaction and type of catalyst were determined. When the ratio of sulfuric acid to the ester was varied from 1.9–6.5 to one mole, a maximum combined yield of 54% of both acid (28%) and ester (26%) was obtained at a ratio of 2.5–3.6 to one. Selected data are given in Table I. When the temperature was varied, it was found that room temperature (20–30°) was the most satisfactory for the condensation. At 0° the condensation proceeds too slowly, and at 100° the reactants are apparently destroyed. At 42° the yields are slightly lower than those obtained under comparable conditions at room temperature as indicated in Table II. The data in Table III demonstrate that there is no advantage in extending the reaction beyond 5 or 6 days. For extremely long reaction periods the yield actually decreases. The use of aluminum chloride or boron trifluoride etherate gave lower yields of the ester and no acid at all.

TABLE I

EFFECT OF CONCENTRATION OF REACTANTS[a]

Ratio[b]	Yield, % Acid	Ester	Total
1.9/1	5	48[c]	53
3.6/1	28	26	54
6.5/1	10	20[c]	30

[a] Time of runs, 15 or 20 days. [b] Moles H_2SO_4/moles acetoacetic ester. [c] Crude yield; b.p. 130–90° at 35 mm.

TABLE II

EFFECT OF TEMPERATURE[a]

Temp., °C.	Yield, % Acid	Ester	Total
0–5	1.5	6.8	8.3
20–30	18	22	40
42	14.8	19.5	34
100	0	0	0

[a] These data are for 28 hours. The mole ratio of sulfuric acid to ethyl acetoacetate is 3.2/1.

TABLE III

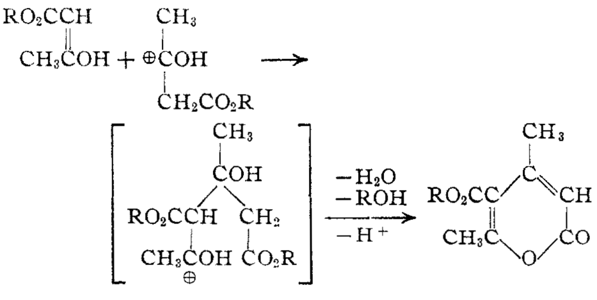
EFFECT OF TIME[a]

Time	Yield, % Acid	Ester	Total
28 hours	18	22	40
2 days	19	29	48
4 days	22	32	54
6 days	25	30	55
15 days	28	26	54
17 days	24	27	51
40 days	15	24	39

[a] Reactions run at room temperature. The mole ratio of sulfuric acid to ethyl acetoacetate varied from 2.5/1 to 3.6/1.

Under all conditions tried both isodehydroacetic acid and ester were obtained together. It was believed that additional information on hydrolysis of isodehydroacetic ester might suggest conditions under which the condensation could be carried out with simultaneous hydrolysis to give the acid as the major product. The data obtained show that isodehydroacetic ester is not easily hydrolyzed. Hydrolysis with concentrated sulfuric acid at elevated temperatures produced isodehydroacetic acid in only 40–50% yields and usually 20–30% of the ester was recovered. From attempts to hydrolyze the ester by 100% sulfuric acid at room temperature, the ester was recovered in 92% yield. When hydrolysis of the ester or esterification of acid was undertaken under the preferred conditions for the condensation, as outlined above, the starting material was recovered and none of the product could be detected. This means that under the preferred conditions for the condensation, any isodehydroacetic ester that is formed will remain unhydrolyzed and that the isodehydroacetic acid which is formed is not formed by hydrolysis of the cyclic ester but by condensation of acetoacetic acid formed by hydrolysis of acetoacetic ester prior to condensation. The best procedure thus far devised for obtaining maximum yields of isodehydroacetic acid is to carry out the condensation so as to obtain the maximum yield of both ester and acid and hydrolyze the ester thus obtained to the acid in a separate step.

The mechanism of this condensation reaction is apparently that of an acid-catalyzed aldol condensation[5] between the carbonyl group of one molecule and the methylene carbon of another molecule followed by lactonization



The formation of isodehydroacetic ester and acid proceed independently and not from one to another, for our data on hydrolysis of isodehydroacetic ester and esterification of isodehydroacetic acid show that the ester is not hydrolyzed nor the acid esterified under the conditions of the condensation. This indicates that the acetoacetic ester itself is in part hydrolyzed prior to condensation and undergoes condensation as the free acid to form isodehydroacetic acid and ester.

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(2) A. Hantzsch, *Ann.*, **222**, 9 (1883).

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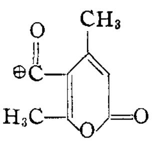
The fact that ethyl isodehydroacetate is not rapidly hydrolyzed and the acid not rapidly esterified in concentrated sulfuric acid provides an interesting basis for a preliminary comparison of the degree of resonance stabilization in the ion I with that in the 2,6-dimethylbenzoyl carbonium ion, II. 2,6-Dimethylbenzoic acid is known to have a van't Hoff *i* factor of more than three in sulfuric acid[6] and this fact has been interpreted as due to partial dissociation into ions stabilized by resonance through electron-releasing characteristics of the two, one is not enough, ortho methyl groups. This effect has been used to explain the van't Hoff factor of nearly four in concentrated sulfuric acid and the ease of hydrolysis of ethyl 2,4,6-trimethylbenzoate in 100% sulfuric acid. That this effect is not necessarily steric is indicated by the fact that 2,4,6-tribromobenzoic acid is not rapidly esterified as is the corresponding trimethyl derivative.[7]



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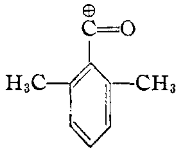

II

Apparently, the two ortho methyl groups in the pyrone do not contribute sufficiently to the resonance stabilization of the ion I to promote facile esterification and hydrolysis as observed in the 2,4-6-trimethylbenzoate types but one would not predict that the two methyl groups of the pyrone would produce the same ease of hydrolysis observed with ethyl trimethylbenzoate. Precise data are unavailable for comparing ease of hydrolysis or esterification or van't Hoff *i* factors of the *o,o'*-dimethyl-1,2-pyrone and the 2,6-dimethylbenzenecarboxylic acids. It appears likely, however, that such data will provide the basis for a quantitative comparison of the degree of resonance stabilization of the benzene and pyrone rings in concentrated sulfuric acid although it is recognized that the pyrone may exist as a conjugate acid or perhaps even undergoes reversible ring opening under these conditions. These, as well as data relating other heterocyclic types, are being obtained and will be reported in following papers.

Along with these studies, we have confirmed the saponification of isodehydroacetic ester to *β*-methylglutaconic acid[2,8] in 88% yield and observed that hydrolysis of ethyl 3-bromoisodehydroacetate is accompanied by decarboxylation with resultant formation of 3-bromo-4,6-dimethylpyrone and that hydrolysis of ethyl 3-nitroisodehydroacetate is accompanied by extensive decomposition.

Experimental

All melting points and boiling points are uncorrected.

Preparation of Isodehydroacetic Acid and Ester.—The general procedure previously described[3] was followed for the sulfuric acid condensation of ethyl acetoacetate to isodehydroacetic acid. Variations of this procedure are given in Tables I, II and III. The yields indicated therein are for isodehydroacetic acid, m.p. 155°, and ethyl isodehydroacetate boiling over a 5° range under reduced pressure except as noted. The following is a brief description of the procedure.

The sulfuric acid was cooled in an ice-bath and the acetoacetic ester added at a temperature of 10–15°. The reaction mixture was protected from atmospheric moisture and allowed to stand at the times and temperatures indicated. After pouring on ice, the products were extracted with ether and the isodehydroacetic acid separated by extracting the ether with sodium carbonate solution. Acidification with excess hydrochloric acid precipitated the crude acid, which was recrystallized from water. The ester was distilled under reduced pressure, after removal of the ether.

Attempts to use other acidic catalysts gave smaller yields of the condensation products. Using aluminum chloride, a 27.5% yield of ethyl isodehydroacetate alone was obtained, while boron trifluoride–etherate gave only a 20% yield of the ester.

Hydrolysis of Ethyl Isodehydroacetate.—The isodehydroacetic ester was hydrolyzed to isodehydroacetic acid by heating with 5 times its weight of concentrated sulfuric acid on a steam-bath for 4 to 5 hours. This was worked up to give a 40–50% yield of isodehydroacetic acid and a 20–30% recovery of the original ester. When the ester was dissolved in 100% sulfuric acid and poured onto ice after standing at room temperature, the original ester was recovered. No isodehydroacetic acid was detected.

Acid hydrolysis of 3-bromoisodehydroacetic acid ethyl ester,[2] produced a mixture consisting of 3-bromo-4,6-dimethylpyrone, m.p. 105°,[2] in 27% yield and 3-bromoisodehydroacetic acid, m.p. 160–2°,[9] in 11% yield. 3-Nitroisodehydroacetic ester under similar conditions underwent extensive decomposition from which no identifiable products were obtained.

Attempted Esterification and Hydrolysis at Room Temperature.—In order to determine whether the acid was formed from the ester or *vice versa*, in conditions used in the condensation, attempts to hydrolyze the ester at room temperature and to esterify the acid in concentrated sulfuric acid were made. When the ester was allowed to stand for 3 days in sulfuric acid at room temperature, 92% of the original ester was recovered and no acid detected. From a mixture of isodehydroacetic acid, ethanol and sulfuric acid there was obtained an 81% recovery of the acid and no ester.

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Preparation of Acetyl-L-leucine and Acetyl-L-glutamic Acid

BY HANS WOLFF AND ARTHUR BERGER

The use of ketene as acetylating agent for *α*-amino acids was proposed by Bergmann and Stern,[1] who prepared N-acetyl-*dl*-leucine from *dl*-leucine by treating its water solution with ketene and N-acetyl-*l*-glutamic acid by passing ketene through an aqueous solution of sodium *l*-glutamate. Cahill and Burton[2] have claimed that acetylation of the active amino acids *l*-leucine and *l*-glutamic acid with ketene leads to complete racemization when carried out under acid conditions but that no racemization occurs as long as the solution is kept alkaline. The acidity obtained by the generation of acetic acid from ketene and water in excess of the alkali added to the reaction mixture was found to be sufficient to cause rapid racemization. Racemization occurs on acetylating *α*-amino acids with excess acetic anhydride in glacial acetic acid as reported by Bergmann and Zervas[3] and confirmed in our experiments.

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[2] Cahill and Burton, *J. Biol. Chem.*, **132**, 161 (1940).

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