and that the phase had a narrow homogeneity range and only a small degree of intrinsic disorder. The difficulty concerning the correct formula seems to have been resolved recently by Geller (6), who obtained the crystal structure of the phase and found by crystallographic argument that the true primitive formula should be $Rh_{17}S_{15}$. Since our experimental work was done before the publication of Geller's results, we had been unaware of the correct formula and therefore selected the compositions Rh_8PdS_8 and Rh_8AgS_8 on the assumption that the coordination situation in $\rho(Rh,S)$ was similar to that in $\pi(Co,S)$. Since this now has been shown not to be the case, nothing can be said at present about the nature of the Pd substitution in the $\rho(Rh,S)$ structure, apart perhaps from a speculation that the palladium atoms would tend to prefer square planar coordination and thus might locate in the 3(d) sites of the Pm3m structure proposed by Geller. Ibrahim (7) prepared, in this laboratory, as early as 1957 a number of compositions of the type $\pi(Co,Rh,S)$ and these are now being examined in the light of the tetrahedral, octahedral, and square planar coordination preferences.

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MONOFLUOROSUCCINIC ACID¹

F. H. DEAN AND F. L. M. PATTISON

Monofluorosuccinic acid, HOOCCH₂CHFCOOH, is an interesting compound from a biochemical standpoint, because it is one of the few remaining monofluorinated members of the tricarboxylic acid cycle which has not yet been authenticated; as such, its action on the enzymes of the cycle would be significant in the general study of poisoning by organic fluorine compounds.

Mention has been made of this acid on several occasions. Martius (2), in 1949, reported experiments using monofluorosuccinic acid; he thanked Professor Theilacker for a gift of the acid, but no details of its preparation have appeared in the literature. In 1953, Gitter, Blank, and Bergmann (3) stated that the sodium salt is non-toxic, but gave no indication of the source nor of the method of preparation of the material tested. In 1956, Bergmann and Szinai (4) reported the preparation of an impure sample of diethyl monofluorosuccinate by reaction of the enolate of ethyl fluoroacetate with ethyl bromoacetate;

¹First reported at the Second International Symposium on Fluorine Chemistry, Estes Park, Colorado, July 17-20, 1962(1).

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the analysis was in error, and the authors stated that the ester could not be obtained in a pure condition. Hydrolysis of this crude material did not yield the free acid by the procedures used. Finally, Peters (5), a year later, called attention to the unconfirmed results of Martius and questioned the identity of the test sample, "as several others (personal communication) have not been successful in preparing monofluorosuccinic acid".

We now wish to report the preparation of this acid from diethyl succinate by the following route:



The method involves the addition of the ethoxalyl grouping, which in turn promotes fluorination (6) by perchloryl fluoride. The strongly electronegative character of the fluorine atom thus introduced greatly facilitates the alkaline cleavage of the resulting non-enolizable β -keto-ester. Under the very mild reaction conditions, beta-elimination of hydrogen fluoride becomes negligible. In short, the activating ethoxalyl grouping is preferentially removed. The overall yield of diethyl monofluorosuccinate, based on the potassium enolate of triethyl oxalylsuccinate, was 73%; the acid hydrolysis of this ester to monofluorosuccinic acid proceeded in 67% yield.

The intermediate ester, triethyl α -fluoro- α -oxalylsuccinate, could not be purified by distillation, even at 0.05 mm pressure, because of ready decarbonylation. Under these conditions, diethyl α -fluoro- α -carbethoxysuccinate was formed in 77.5% yield:



Monofluorosuccinic acid and its diethyl ester were found to be non-toxic to mice by intraperitoneal injection in propylene glycol ($LD_{50} > 107 \text{ mg/kg}$). The acid is being examined in other laboratories for its biochemical properties.

EXPERIMENTAL

Melting points (uncorrected) were determined on a Kofler hot stage, and densities with a Fisher-Davidson gravitometer. The nuclear magnetic resonance spectrum was obtained with a Varian DP-60 spectrometer. Infrared spectra were obtained with a Beckman IR-7 infrared spectrophotometer (in the case of diethyl monofluorosuccinate) or with an IR-5 (in the case of monofluorosuccinic acid and diethyl α -fluoro- α -carbethoxysuccinate). The perchloryl fluoride was purchased from the Technical Division of Pennsalt Chemicals Corporation, Philadelphia 18, Pa.

Potassium Enolate of Triethyl Oxalylsuccinate

The potassium enolate was prepared by the standard procedure (7) with two modifications: (a) the work was carried out in a nitrogen atmosphere; and (b) the freshly cut potassium was not washed with ether. By this means, the formation of potassium hydroxide and carbonate was reduced. Diethyl succinate was freshly redistilled through a 23-plate spinning band column (b.p. 97° at 8 mm, n_D^{25} 1.4185, d_4^{20} 1.035). Diethyl oxalate was similarly purified (b.p. 76° at 10 mm, n_D^{25} 1.4090, d_4^{20} 1.075). The super-dry ethanol was stored over Linde molecular sieves, Type 5A. The enolate was washed with dry ether and placed in a P₂O₅ vacuum desiccator for 15 hours at 0.5 mm. Yield: 91–97%, as a light yellow, friable solid.

Diethyl Monofluorosuccinate

A 500-ml three-necked flask was equipped with a stirring magnet, a gas-inlet tube with a fritted-glass gas disperser, a drying tube filled with indicating Drierite, and a -50° to $+50^{\circ}$ thermometer secured by

gum-rubber tubing to a ground-glass holder. After the flask had been flushed with dry nitrogen, dry potassium enolate (23.6 g, 75.5 mmoles) was introduced, followed by super-dry ethanol (300 ml). To the mixture was added 2 ml of bromthymol blue (0.05% in absolute ethanol) and dry reagent-grade potassium bicarbonate (1.75 g, 17.5 mmoles). Dry nitrogen was passed through the mixture, which was stirred and cooled in an ice bath. When the temperature was steady at 4°, the perchloryl fluoride cylinder was attached to the gas disperser by gum-rubber tubing² and wired on securely. Perchloryl fluoride gas was then introduced until the temperature had risen to 8-10°. The gas flow was then stopped until the temperature had again fallen to 4°, when it was resumed. In this manner, 10.7 g (104.3 mmoles) of perchloryl fluoride were added over a 1-hour period, the actual duration of gas inflow being 21 minutes. As the perchloryl fluoride is being added, the original deep-green color lightens due to the formation of potassium chlorate; the end of the reaction is readily determined by a color change from green to yellow and by a fall in temperature on the addition of more perchloryl fluoride. The gas cylinder was then detached, an additional quantity (10.2 g, 102 mmoles) of potassium bicarbonate was added, the ice bath was removed, and the mixture was stirred at room temperature (20 hours). The flask was flushed with nitrogen to remove any unreacted perchloryl fluoride, water (800 ml) was added, and the solution was thoroughly extracted with ether. The combined ether extracts were washed with water and dried over magnesium sulphate. The ether was removed on a water bath and the alcohol at aspirator pressure. The residue was then distilled through a 6-in. Vigreux column under oil-pump pressure. Two main fractions were obtained: (a) diethyl oxalate (4.15 g), b.p. 72° at 9 mm to 62° at 2.75 mm, n_D²⁵ 1.4092-1.4090; and (b) diethyl monofluorosuccinate (15.0 g), b.p. 75° at 2.75 mm to 72° at 0.25 mm, $n_{D^{25}}$ 1.4135–1.4133. The first fraction, on redistillation through a spinning-band column, gave 3.23 g of pure diethyl oxalate, b.p. 72° at 8 mm, $n_{D^{25}}$ 1.4087, $d_{4^{20}}$ 1.076, the infrared spectrum of which was identical in all respects with that of a sample of the pure ester.³ Redistillation of the second fraction, which contained about 8% of diethyl maleate (ultraviolet analysis), through the spinning-band column gave pure diethyl monofluorosuccinate (10.6 g, 73%) as a stable, colorless liquid, b.p. 72° at 1 mm, np²⁵ 1.4125, d₄²⁰ 1.142, MR_D 41.98 cc/mole; estimated 42.19 cc/mole. (Gitter, Blank, and Bergmann (3) report b.p. 70-71° at 0.8 mm, np²³ 1.4240, d₄²³ 1.1090, MRp 44.23 cc/mole.) Principal infrared bands (3%) solution in CCl₄), cm⁻¹: 1769.5 (C=O) s, 1746.5 (C=O) s, 1372.8 (CH₃) s, 1286.0 (C-O) s, 1264.0 m, 1179.5 (C-O) s, 1097.0 (C-F) s, 1051.2 m, 1028.5 s. Nuclear magnetic resonance spectrum (27.7% w/v in CCl₄ using tetramethylsilane as internal standard): chemical shifts (τ), coupling constants (c/s). Two CH₃CH₂O: 8.69 τ , 8.73 τ (t); 5.78 τ , 5.85 τ (q); J_{HH} 7.0 c/s. CH₂: 7.17 τ ; J_{HH} 5.9 c/s; J_{HF} 23.3 c/s. CHF: 4.85 τ ; J_{HH} 5.9 c/s; J_{HF} 47.6 c/s. The ester showed only weak end-absorption in the *ultraviolet*, ϵ_{220} 100.5 in 95% ethanol, indicating the absence of diethyl maleate (ϵ_{220} 6380); cf. diethyl succinate, ϵ_{220} 118. Anal. Calc. for C₈H₁₃FO₄: C, 49.99; H, 6.82; F, 9.89. Found: C, 50.16; H, 6.75; F, 9.77.

Monofluorosuccinic Acid

Pure diethyl monofluorosuccinate (3.3 g, 17.1 mmoles) and 5% sulphuric acid (20 ml) were heated under reflux at 110° for 30 minutes, that is, until the mixture appeared to be homogeneous. The cooled solution was extracted once with 35–60° petroleum ether, to remove any unchanged ester, and then was subjected to continuous ether extraction for 38 hours; no further acid was obtained after a further 24 hours of extraction. The extract was dried (magnesium sulphate), filtered, and concentrated using a Rinco rotary evaporator. The addition of benzene (5 ml) and removal of residual ether by boiling induced the acid to crystallize (1.33 g), m.p. 140–147°. Concentration of the mother liquors gave a further quantity (193 mg) of the crude acid. The petroleum ether extract gave 90 mg of unchanged ester. Yield of crude acid (1.523 g) based on ester consumed: 67%. It is important that any residual ester be removed and that the ether solution be dry to avoid difficulties in the initial crystallization of the acid. The acid may be recrystallized from benzene– ether, or, better, from hot ethyl acetate. An analytical sample is conveniently obtained by sublimation at 105° (0.3 mm) as a colorless, crystalline solid, m.p. 144–145°; positive fluorine test. The infrared spectrum in acetonitrile showed a band at 1747 cm⁻¹ (C=O) with a shoulder on the high-frequency side; cf. succinic acid, 1744 cm⁻¹. Ultraviolet absorption spectrum in 95% ethanol (1-mm cells): λ_{max} 198 m μ , ϵ_{max} 130 (cf. maleic acid: λ_{max} 203 m μ , ϵ_{max} 14,900). Anal. Calc. for C₄H₈FO₄: C, 35.30; H, 3.70. Found: C, 35.48; H, 3.72.

Diethyl α -Fluoro- α -carbethoxysuccinate

Attempted distillation of the crude intermediate triethyl α -fluoro- α -oxalylsuccinate at 160–200° (0.05 mm) yielded the decarbonylated ester (77.5%). Redistillation gave a colorless liquid, b.p. 107–109° at 0.55 mm, n_D^{25} 1.4264. The infrared spectrum in CCl₄ showed bands at 1745 (C=O) and 1095 (C-F) cm⁻¹. Anal. Calc. for C₁₁H₁₇FO₆: C, 49.99; H, 6.49. Found: C, 50.13; H, 6.64.

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²Rubber containing carbon black may explode in contact with perchloryl fluoride.

⁸The formation of diethyl oxalate in this process may be explained by solvolytic cleavage of the intermediate triethyl α -fluoro- α -oxalylsuccinate.

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THE RATIO OF THE INDEPENDENT FORMATION CROSS SECTIONS OF THE **ISOMERIC STATES OF Cs134 IN THE PROTON-INDUCED FISSION OF URANIUM**¹

I. H. DAVIES² AND L. YAFFE

Both Cs^{134m} (2.9 hr) and Cs^{134g} (2.1 yr) are formed in the proton-induced fission of uranium. The 2.9-hr metastable state is a primary product shielded by stable Xe¹³⁴ and Ba¹³⁴. The 2.1-yr ground state is formed both as a primary product and from the decay of the metastable state by isomeric transition.

This nuclide provides one of the rare instances where the independent formation cross sections of a pair of isomers produced in fission can be conveniently measured.

In the course of work on the nuclear charge dispersion in the fission of natural uranium by high-energy protons (1), data were collected on the independent yields of cesium isotopes. This enabled us to calculate the ratio of the formation cross sections of the Cs134 isomers at a number of incident proton energies. Details of the separations and measurements are provided in the former work (1).

The β -activity of the cesium fraction, purified radiochemically, was measured by means of an end-window gas-flow proportional counter. The decay curves were resolved cleanly into three components, 32-min Cs¹³⁸, 2.9-hr Cs¹³⁴, and 12.9-day Cs¹³⁶, with a long-lived, low-activity tail. The γ -spectrum of this sample revealed two photopeaks attributable to Cs^{134} (2.1 yr) and Cs^{137} (30 yr) after the decay of Cs^{136} . Both the Cs^{134m} and the Cs^{134} activities were measured relative to that of Cs¹³⁶ from the β - and γ -ray measurements respectively. The independent yield of Cs^{134g} was obtained by difference between the two measurements. The method of calculation of the formation cross sections and the correction factors used are given in the charge dispersion paper (1).

The ratio of the isomeric cross sections as a function of incident proton energy is shown in Fig. 1. It is apparent that the high-spin metastable state (8-) is always favored in this

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