shifted to the violet than with the ether system (*i.e.*, iodine in methanol was orange-brown, addition of fractional amounts of hydrogen fluoride gave orange-red solutions, and this color persisted over a large range of HF–methanol mixture compositions; a violet coloration appeared at higher methanol concentrations than in the ether system).

A noticeable characteristic of the system was the difference in solubility of iodine in the oxygenated solvents and in hydrogen fluoride. Starting with even a dilute solution of iodine in methanol, addition of hydrogen fluoride to about 75% by weight precipitated iodine, and precipitation continued with further addition of hydrogen fluoride. Iodine dissolves slowly in pure hydrogen fluoride.

Some question might be raised concerning the relatively small effects of the lower concentrations of the oxygenated electron donors on the iodine spectrum. It should be pointed out that hydrogen fluoride will compete with the iodine for the electrons of the donor, so that the effective concentration of the latter is considerably diminished. From the evidence as a whole it does not seem that hydrogen fluoride interacts significantly with iodine dissolved in it.

Visual observations and solution make-up were performed with test-tubes formed of fluoride-resistant aluminum phosphate glass ("Fluorex"). The experimental procedures for following absorption spectra in liquid hydrogen fluoride will be described elsewhere.[12]

(12) J. J. Katz and H. H. Hyman, *Rev. Sci. Instruments*, to be published.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Significance of Fungus Growth in Analytical and Radiochemical Work with Strontium-containing Solutions[1]

BY S. Z. LEWIN, PETER J. LUCCHESI AND JOHN E. VANCE

Dipping-type Geiger–Mueller tubes employed in an investigation of rates of dissolution of radioactively-labeled crystals of strontium sulfate in distilled water were observed, in runs at room temperature, to acquire an activity which increased regularly with time. The activity was in the form of an adherent deposit on the surface of the tube, for when removed from the solution and rinsed repeatedly with water, the tube gave practically the same high count as it had when immersed in the solution. The activity recorded by the tube did not decrease at all when the tube was left immersed in a large volume of a solution containing a high concentration of stable Sr^{++}, showing that the radioactive strontium deposited on the tube does not enter into exchange with strontium ions in solution. Firm wiping of the tube removed a large part of the activity, but vigorous scrubbing with a mild abrasive was necessary to remove the remainder. The same effects were observed with glass, stainless steel, and

glyptal-coated dip tubes at room temperature, but they were no longer observed when the experiments were carried out at temperatures near $0°$.

These observations suggested that the deposit on the G–M tube might be a fungus capable of ingesting strontium. To test this hypothesis, the solution from one of the runs (consisting of two liters of water approximately saturated with $Sr^{89}SO_4$) was made 0.5% in dextrose, and set aside for one month at room temperature. A luxuriant growth of mold mycelium was present at the end of this period; it was filtered, air-dried and measured for radioactivity. A 0.24-g. sample of the mold mycelium gave 937 ± 10 counts per minute over background; the same weight of the solution gave 5 c.p.m.

The effect of $SrSO_4$ on the rate of growth of the fungus was investigated by preparing a number of 1% dextrose solutions, half of which were saturated with strontium sulfate, and inoculating all with equal amounts of the mold mycelium obtained as described above. After one day, the solutions containing $SrSO_4$ were decidedly more turbid, due to the mold, than the other solutions; after one month, the strontium-containing solutions had large colonies of mycelium which did not adhere to the walls of the flask, whereas the solutions containing the same nutrient, but no $SrSO_4$, showed only a thin growth which adhered firmly to the glass surface.

The fungus, when cultured on bread slices, produced black colonies having the appearance characteristic of *Rhizopus nigricans*. It is concluded that this mold grows in solutions of strontium sulfate (even when the only nutrient available is what falls into the solution from the laboratory air), that its growth is actually accelerated by the presence of the Sr^{++}, and that it ingests strontium and incorporates it into its structure in a form that does not exchange with strontium ions in solution.

Analyses of solutions of $SrCl_2$ and $SrSO_4$ in water by a colorimetric procedure[2] show that the concentration of strontium ions in these solutions may decrease considerably with time; for example, a 0.06% solution of $SrCl_2$ in distilled water in a glass-stoppered flask decreased in concentration by about 60% over a three-month period.

It follows that the possibility of loss of Sr^{++} due to fungus activity must be considered in all analytical and radiochemical work with strontium-containing solutions.

(2) P. J. Lucchesi, S. Z. Lewin and J. E. Vance, *Anal. Chem.*, in press.

CHEMISTRY DEPARTMENT
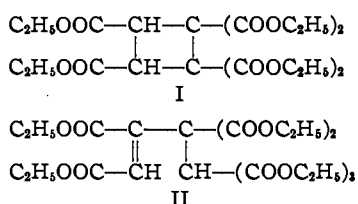NEW YORK UNIVERSITY
NEW YORK 3, N. Y.

The Preparation of Ethyl 1,1,2,2,3,4-Butene-3-hexacarboxylate

BY C. G. OVERBERGER AND PETER KABASAKALIAN

In connection with other work, we attempted to synthesize ethyl 1,1,2,2,3,4-cyclobutanehexacarboxylate (I). Reid and Sack[1] have recently re-

(1) E. B. Reid and M. Sack, THIS JOURNAL, **73**, 1985 (1951).

ported an attractive synthesis for this ester. Repetition of this synthesis however has revealed that this reported product is actually its precursor, ethyl 1,1,2,2,3,4-butene-3-hexacarboxylate (II).

$$C_2H_5OOC—CH—C—(COOC_2H_5)_2$$
$$C_2H_5OOC—CH—C—(COOC_2H_5)_2$$
I

$$C_2H_5OOC—C——C—(COOC_2H_5)_2$$
$$C_2H_5OOC—CH　CH—(COOC_2H_5)_3$$
II

Chromatographic analysis of the product resulting from this procedure on a Florisil column indicated that the material was homogeneous. The infrared absorption spectrum was found to be identical to the one obtained by Reid and Sack.[1] A carbon–carbon double bond absorption was present at 1635 cm.$^{-1}$. The ultraviolet absorption spectrum had an approximate maximum at 208 mμ with ϵ of 7,600 indicative of an α,β-unsaturated ester. At 208 mμ, the ϵ of ethyl maleate is 6,800; ethyl fumarate, 17,600, and ethyl ethylenetetracarboxylate, 11,200. The accuracy of these values is not completely satisfactory due to the accuracy of the instrument at 208 mμ; however, the approximate values obtained strongly support structure II.

Polarographic reduction gave a diffusion current which indicated the presence of one conjugated double bond per mole of ester. This was determined by comparing the diffusion current with those obtained for ethyl maleate, ethyl fumarate and ethyl ethylenetetracarboxylate. Ozonolysis gave oxalic acid in 40% yield. Only structure II is consistent with this evidence.

Experimental

Ethyl 1,1,2,2,3,4-Butene-3-hexacarboxylate (II).—Ethyl acetylenedicarboxylate was treated with ethyl 1,1,2,2-ethanetetracarboxylate in the presence of sodium ethoxide according to the procedure of Reid and Sack.[1] Ethyl 1,1,-2,2,3,4-butene-3-hexacarboxylate (II) was isolated contaminated with ethyl ethanetetracarboxylate. The separation of starting material from product was only accomplished by successive fractional crystallization from 80% ethanol, the starting material being more insoluble. In a typical experiment a 50% yield of starting material, the ethanetetracarboxylate, m.p. 74–76°, was recovered, along with product. Recrystallization of the crude product gave a 16% yield, m.p. 77–78°. Anal. Calcd. for $C_{22}H_{32}O_{12}$: C, 54.10; H, 6.56. Found: C, 54.43; H, 6.66; mol. wt., 455 (cryoscopically in benzene).

Proof that starting material was obtained in 50% yield was afforded by a mixed melting point 74–76° and a comparison of the infrared spectra which were identical.

Ozonolysis of Ethyl 1,1,2,2,3,4-Butene-3-hexacarboxylate (II).—The method of Farmer, Gosal and Kon[2] was followed, who ozonized compounds of a similar type, for example, ethyl-α-carbethoxy-α-methyl aconitite. Ozonolysis was carried out for 13 hours with ca. 6% ozone (oxygen flow 1 liter/min.). The oxalic acid was isolated as calcium oxalate monohydrate in 40% yield (by titration). Liberation of the oxalic acid from the calcium salt with sulfuric acid followed by ether extraction gave crystalline oxalic acid, m.p. 189° dec.

Physical Data.—Infrared spectrum of a Nujol mull was determined with a Perkin–Elmer model 21 recording spectrophotometer with a sodium chloride prism.

Ultraviolet absorption measurements were determined on

(2) E. H. Farmer, S. C. Gosal and G. A. R. Kon, *J. Chem. Soc.*, 1804 (1936).

methanolic solutions with a Cary recording spectrophotometer, model 11.

Polarographic measurements on 0.001 M solutions in 50% ethanol (0.1 N KCl as electrolyte) were made using the Sargent recording polarograph, model XXI.

(3) E. B. Reid, *Chem. and Ind.*, **32**, 846 (1953).

DEPARTMENT OF CHEMISTRY
INSTITUTE OF POLYMER RESEARCH
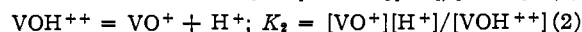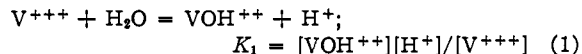POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 2, N. Y.

Equilibria in Solutions of +3 and +4 Vanadium

BY LOUIS MEITES

In the course of some other work it became essential to secure estimates of the hydrolysis constants of vanadium in its +3 and +4 oxidation states. While the data for these calculations have been available for some years,[1] an error in their original interpretation has led to the belief that they cannot be used for this purpose. Since the constants themselves are of some interest and the method used in their derivation, though rather simple, appears not to have been previously described or used, it seems desirable to offer a brief account of our method and conclusions.

Vanadic ion, V^{+++}, hydrolyzes in two steps[2,3]

$$V^{+++} + H_2O = VOH^{++} + H^+;$$
$$K_1 = [VOH^{++}][H^+]/[V^{+++}] \quad (1)$$
$$VOH^{++} = VO^+ + H^+; K_2 = [VO^+][H^+]/[VOH^{++}] (2)$$

Now

$$[V^{+++}] + [VOH^{++}] + [VO^+] = c \quad (3)$$

where c is the total analytical concentration of +3 vanadium, and the stoichiometry of the reactions gives

$$[H^+] = [VOH^{++}] + 2[VO^+] \quad (4)$$

Combining equations 3 and 4 and expressing $[V^{+++}]$ and $[VO^+]$ in terms of $[VOH^{++}]$ gives

$$[VOH^{++}]([H^+]^2 - K_1K_2)/K_1[H^+] = c - [H^+] \quad (5)$$

Equations 2 and 4 give

$$[VOH^{++}] = [H^+]^2/([H^+] + 2K_2) \quad (6)$$

Eliminating $[VOH^{++}]$ from equations 5 and 6 yields, finally

$$(c - [H^+])/[H^+] = ([H^+]^2 - K_1K_2)/(K_1[H^+] + 2K_1K_2) \quad (7)$$

Rearranging and differentiating, we secure

$$[H^+](\Delta[H^+]^2/\Delta(c - [H^+])) = K_1[H^+] + 2K_1K_2 \quad (8)$$

Values of the term $\Delta[H^+]^2/\Delta(c - [H^+])$ are secured from a large-scale plot of $[H^+]^2$ *vs.* $(c - [H^+])$ by measuring the slope of the tangent to the curve at each experimental point. These slopes, when multiplied by the corresponding values of $[H^+]$, give values of the right-hand side of equation 8.

(1) G. Jones and W. A. Ray, THIS JOURNAL, **66**, 1571 (1944).
(2) J. J. Lingane and L. Meites, *ibid.*, **70**, 2525 (1948).
(3) S. C. Furman and C. S. Garner, *ibid.*, **72**, 1785 (1950).