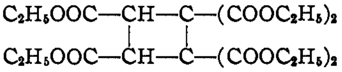
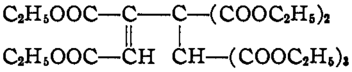
ported an attractive synthesis for this ester. Repetition of this synthesis however has revealed that this reported product is actually its precursor, ethyl 1,1,2,2,3,4-butene-3-hexacarboxylate (II).



$$\begin{array}{l}\mathrm{C_2H_5OOC{-}CH{-}C{-}(COOC_2H_5)_2}\\ \qquad\qquad\quad |\qquad\ \ |\\ \mathrm{C_2H_5OOC{-}CH{-}C{-}(COOC_2H_5)_2}\end{array}$$

I



$$\begin{array}{l}\mathrm{C_2H_5OOC{-}C{-\!-}C{-}(COOC_2H_5)_2}\\ \qquad\qquad\quad \|\qquad\ \ |\\ \mathrm{C_2H_5OOC{-}CH\ \ CH{-}(COOC_2H_5)_2}\end{array}$$

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 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.

Acknowledgment.—Dr. E. B. Reid independently has recently obtained other evidence to substantiate structure II, which has been published elsewhere.[3] We are grateful to Dr. Reid for his cooperation and help.

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

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

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Equilibria in Solutions of +3 and +4 Vanadium

BY LOUIS MEITES

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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]

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

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

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.

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[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).

These, when plotted against the concentration of hydrogen ion, should give a straight line whose slope is equal to K_1 and whose zero intercept is equal to $2K_1K_2$. Such a plot is shown as Fig. 1: from it we conclude that the hydrolysis constants of vanadic ion are

$$K_1 = [VOH^{++}][H^+]/[V^{+++}] = (1.2 \pm 0.3) \times 10^{-3}$$
$$K_2 = [VO^+][H^+]/[VOH^{++}] = (3 \pm 1.5) \times 10^{-4}$$

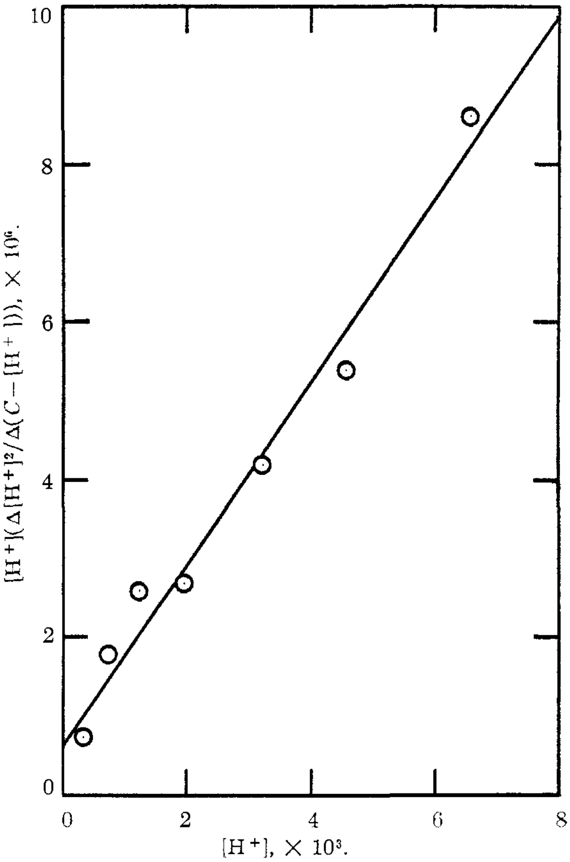

Fig. 1.—Plot of $[H^+](\Delta[H^+]^2/\Delta(c - [H^+]))$ *vs.* $[H^+]$ for the data of Jones and Ray on the *p*H values of vanadic sulfate solutions at concentrations between 0.0004 and 0.040 *M* in +3 vanadium.

The data on which these calculations were based were secured by Jones and Ray,[1] who measured the *p*H values of solutions of carefully purified vanadic sulfate at a number of concentrations from 0.0001 to 1 *M* in +3 vanadium. They assumed that VO^+ was the only hydrolysis product and attempted to compute a hydrolysis constant from their data, but failed because their equations could not correctly describe the relationship between the concentration of hydrogen ion and that of unhydrolyzed vanadic ion.

Two assumptions were made in these calculations: that the measured *p*H is equal to $-\log[H^+]$, and that all activity coefficients may be set equal to unity. In the range of ionic strengths used in constructing Fig. 1, these assumptions probably do not lead to errors much greater than those corresponding to the uncertainties in the data themselves.

In addition to its use in the calculation of consecutive hydrolysis constants, this method is in principle also suitable for the calculation of the dissociation constants of any dibasic acid from data on $[H^+]$ and *c*. In practice, however, it is useful only if K_1 and K_2 are not too widely separated: if this is not the case, the terms representing the contribution of the second dissociation or hydrolysis step become relatively very small and the experimental errors are enormously magnified in the calculation of K_2.

We have also used the data of Jones and Ray[1] on the *p*H values of vanadyl sulfate solutions to calculate the hydrolysis constant of VO^{++}. As the calculations are perfectly straight-forward, we shall record only the final result. For $0.0001 \leqslant c \leqslant 0.050$

$$K = [VOOH^+][H^+]/[VO^{++}] = (4.4 \pm 0.4) \times 10^{-6}$$

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Some Observations on High Temperature Gallate (III) Formation

BY THERALD MOELLER AND GLENDALL L. KING

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Physicochemical studies[1] on gallium(III) salt solutions have shown the gallium ion to be comparatively acidic. Further information on the acidic properties of gallium in this oxidation state might be expected from investigations of reactions of the oxide with more basic oxides and hydroxides. Although gallate(III) formation in aqueous solution is well recognized,[1,2] the species present are somewhat difficult to characterize. On the other hand, high temperature reactions yield easily studied products. The preparation and properties of spinel-like gallates of the type $M^{II}Ga_2O_4$, where M^{II} is magnesium,[3,4] zinc[5] or cadmium,[6] have been described. These observations have been checked and extended to materials derived from other basic oxides. All products have been examined by X-ray diffraction techniques.

Experimental

Gallium metal, containing only spectroscopic traces of impurities, was converted to the oxide by dissolution in acid, precipitation with ammonia, and ignition. Weighed samples (0.05–0.10 g.) of gallium(III) oxide were sintered with sufficient quantities of various chemically pure metal oxides or nitrates to give 1:1 mole ratios of the two oxides. Heating was effected in porcelain containers, the conditions being summarized in Table II. The cooled products were stirred thoroughly and sampled carefully for X-ray diffraction studies. Powder patterns were obtained with Hayes powder diffraction cameras of 7 cm. radius, using Machlett,

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[1] T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1950).

[2] B. N. Ivanov-Emin and Ya. I. Rabovik, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 781 (1944).

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[4] F. Machatschki, *Z. Krist.*, **82**, 348 (1932).

[5] F. Buschendorf, *Z. physik. Chem.*, **B14**, 297 (1931).

[6] W. Rüdorff and B. Reuter, *Z. anorg. Chem.*, **253**, 194 (1947).