Letters to the editor

in Fig. 5, which is completely consistent with all the kinetic and stereochemical aspects of this fascinating process. The proposed mechanism provides an interesting example of an $S_{\rm N}$ be process coupled to an apparent nucleophilic attack at the cobalt(III) atom. The kinetic studies will be reported in detail elsewhere. It should be pointed out, however, that the distinctive (OH⁻) dependence of this rate process provides a pleasing explanation for the fact that only a single (consecutive) rate-determining step occurs. The intervention of an $S_{\rm N}$ be mechanism after co-ordination of the first amino group immediately clarifies the relatively great rate at which the second and third ethylenediamine molecules are added.

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Vanadium (IV) formate

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THE acylates of the transition metals are quite limited in extent. Only the lower valence states of metals in the sixth, seventh and eighth families have been reported. The acetate of titanium is limited to an oxy-salt TiO(OOCCH₃)₂. We have observed the formation of vanadium (IV) formate, $V(OOCH)_4$ resulting from the reaction of anhydrous formic acid with vanadium (III) chloride. The green crystals of this unusual compound readily separate from solution after either VCl₃ or VCl₂ has been refluxed with an excess of acid. It was found convenient to reflux 550 ml of anhydrous formic acid with 100 g of VCl₃ for 64 hr. After separating on a Buchner funnel, the crystals were washed with a polar organic solvent. The product analysed 21.8 per cent vanadium and 20-5 per cent carbon. All of the vanadium appeared in the tetravalent state as determined by titration with ferrous ion in the presence of diphenyl amine sulphonate. The atomic ratio of vanadium to carbon of 1:4-05, the



close comparison with a calculated 22.05 per cent vanadium and 20.8 per cent carbon content and the thermal decomposition data strongly support our assumption of the formula $-V(OOCH)_4$.

Examination of the vanadium formate by Cu radiation X-ray ($K_{\alpha} = 1.54178$) showed a bodycentred cubic structure with eight molecules per unit cell (volume 1643×10^{-24} cm³) and $a_0 =$ 11.80 Å. The refractive index was observed to be 1.61. The calculated density was 1.87. This agrees with the determined density of 1.79, an average of several pycnometric densities using different organic liquids.

The solubility of vanadium (IV) formate is what one would expect. The compound was found to be insoluble (0.03 g/l.) in organic solvents: n-hexane, tetrahydrofuran, ethanol, ethyl ether, acetone

154

and benzene. Its solubility in water was 21.8 g/l. No decomposition was observed in air at room temperature and the compound was not hygroscopic. While the point was not checked, it is our belief that the salt could not be recovered by evaporation of its aqueous solution.

A thermal decomposition curve for vanadium (IV) formate is shown in the figure below. In air, the compound is rapidly converted to V_2O_5 . The reaction starts at 140–160°C, and is complete by 280°C. In argon, decomposition does not begin until about 240°C and the final product is V_2O_4 . In hydrogen, a two-step process was observed.

The first stage is the reduction to $V(OOCH)_3$ beginning slowly below 160° and being completed by 220°. This compound is stable to 280° where rapid conversion to V_2O_3 begins. These decompositions were followed by means of a Stanton recording thermogravimetric balance.

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Infra-red absorption spectra of biuret and its metal complexes

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DURING the course of a study on infra-red absorption spectra of complexes of biuret with bivalent metals, I have found that the biuret molecule exists in at least two forms depending on the recrystallizing conditions. Crystals recrystallized from water (biuret monohydrate) give an infra-red absorption



FIG. 1.—Infrared spectra of biuret. (a), crystals from water (solid line); (b), crystals from alcohol (broken line).

curve shown in Fig. 1, (a), and those from ethanol give a different curve (b). The former and the latter will be called the form α and β . The observed frequencies are shown in Table 1 and the most characteristic bands of each form are designated by * in the table. These curves were obtained in hexachlorobutadiene and in Nujol mulls over their proper regions by means of a Perkin-Elmer Model 21 with sodium chloride and calcium fluoride prisms.

These two forms seem to transform into each other. For example, Fig. 2 shows the changes of characteristic bands in 1800–1200 cm⁻¹; (a) is a spectrum of the α -form taken in Nujol and hexachlorobutadiene mulls and (b) is the one of the same sample taken in a KBr pellet. It is seen that the bands of the β -form appear in the latter curve. After keeping for six days, the same KBr pellet gave almost the same spectrum as (a). No chemical reaction seems to have occurred between biuret and KBr powder, for the bands in a KBr pellet coincide with either those of the α - or β -form taken