

solid dissolved in deuterium oxide (heavy water) containing about 35 per cent sodium deuteroxide (NaOD) (no proton resonance could be observed on the solvent). Again the spectrum consists of only two peaks separated by 14.7 p.p.m. This shows that the solid contains H<sub>2</sub>O or OH<sup>-</sup> groups as well as hydridic protons. The fact that only two peaks occur indicates that alcohol and ethylenediamine are absent, and this is confirmed by chemical tests. The ratio of the intensity of H<sup>-</sup> peak/intensity of H<sub>2</sub>O - OH<sup>-</sup> peak ≈ 2. Hence the ratio H<sup>-</sup>/H<sup>+</sup> in H<sub>2</sub>O or OH<sup>-</sup> ≈ 2; but it must be noted that the sample used in the deuterium oxide experiment had been standing under vacuum for about one month and may have been partially dehydrated.

These observations demonstrate the existence of a soluble rhenium hydride. This is the first example of a soluble transition metal hydride which does not also contain complexing groups such as C<sub>5</sub>H<sub>5</sub><sup>-</sup>, CO or CN<sup>-</sup> attached to the metal ion (biscyclopentadienylrhenium hydride and rhenium carbonyl hydrides are known<sup>3</sup>). We believe that it is now no longer necessary to postulate the existence of the rhenide ion, Re<sup>-</sup>, or an aquo complex of this ion, since all the properties of the apparent (-1)-oxidation state of rhenium<sup>1,2,4</sup> may be explained as being due to a hydride of a positive oxidation state of rhenium. Work on this problem is continuing, and it appears possible that more than one rhenium hydride may exist. Further details will be reported at a later date.

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*Note added in proof.* Two measurements of the area beneath the high-field proton-resonance peak in deuterated basic aqueous solvent gave 7.3 and 6.5 for the ratio of hydridic hydrogen atoms to rhenium atoms in the compound. The measurement, expected to be reliable to about 20 per cent, was calibrated by the addition of a known quantity of normal-isotopic water to the deuterated solvent.

A. P. GINSBERG  
J. M. MILLER  
J. R. CAVANAUGH  
B. P. DAILEY

Department of Chemistry,  
Columbia University,  
New York 27.

<sup>1</sup> Bravo, J., Griswold, E., and Kleinberg, J., *J. Phys. Chem.*, **58**, 18 (1954).

<sup>2</sup> Floss, J. G., and Grosse, A. v., *J. Inorg. Nuclear Chem.*, **9**, 318 (1959).

<sup>3</sup> See, for example, Wilkinson, G., and Birmingham, J. M., *J. Amer. Chem. Soc.*, **77**, 3421 (1955).

<sup>4</sup> Lundell, G. E. F., and Knowles, H. B., *J. Res. Nat. Bur. Stand.*, **18**, 629 (1937); Tomicek, O., and Tomicek, F., *Coll. Czech. Chem. Comm.*, **11**, 626 (1939). Lingane, J. J., *J. Amer. Chem. Soc.*, **64**, 1001, 2182 (1942). Maun, E. K., and Davidson, N., *ibid.*, **72**, 3509 (1950). Ruffs, C. L., and Elving, P. J., *ibid.*, **73**, 3284, 3287 (1951).

### Formation of Volatile Compounds on Gas-Liquid Chromatography Columns

THE communication by Weurman and Dhont<sup>1</sup> reporting the formation of volatile esters on gas-liquid chromatography columns using polyethylene glycol 600 prompts us to report our own findings with a similar stationary liquid phase.

When first preparing a column filling with polyethylene glycol 400, it was distributed on 'Celite 545' in a mixed solvent of acetone and diethyl ether which was afterwards removed by heating in an

oven at 100° C. for 3 hr. During this period a strong smell of formaldehyde was noticed but this later disappeared, and the column was therefore packed and brought into use at 60° C. with nitrogen as carrier gas. The copper connexions of the thermistor detector became corroded and the base line irregular. The stock of polyethylene glycol 400 was afterwards tested and found to contain formaldehyde (chromotropic acid test) and formic acid (paper chromatogram by Dr. G. C. Whiting).

Since this time we have pre-treated the polyethylene glycol 400 as suggested by Adlard<sup>2</sup>, namely, by heating to 100° C., but under a higher vacuum (0.01 mm. of mercury), for 16 hr. Satisfactory results have since been obtained, chromatograms of alcohols showing no abnormalities. It thus seems that polyethylene glycols as supplied by the manufacturers contain volatile impurities which should be removed before use as stationary phases. Our findings offer an explanation of the source of formic acid causing the esterification observed by Weurman and Dhont.

MARGARET E. KIESER  
D. J. SISSONS

Long Ashton Research Station, Bristol.

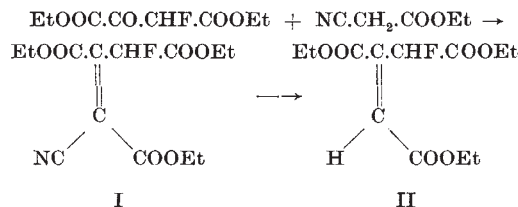
<sup>1</sup> Weurman, C., and Dhont, J., *Nature*, **184**, 1480 (1959).

<sup>2</sup> Adlard, E. R., "An Evaluation of Some Polyglycols used as Stationary Phases for Gas-Liquid Partition Chromatography". Symposium on Vapour Phase Chromatography, Institute of Petroleum, London, May-June, 1956.

### Triethyl α-Fluoroacnitate

THE current theory on the mode of action of fluoroacetate<sup>1</sup> implies the lethal synthesis of fluorocitrate which poisons the enzyme aconitase, thus preventing the catabolism of citrate to aconitate; it seemed of interest to prepare and study α-fluoroacetic acid, HOOC.CHF.C(COOH)=CH.COOH. Triethyl fluorocitrate, which would appear to be a suitable starting material, has been prepared in a facile reaction, namely, by the Reformatsky reaction between diethyl oxalofluoroacetate and ethyl bromoacetate<sup>2</sup>, but our attempts to dehydrate this compound failed to give a defined product.

Better results were obtained by the condensation of diethyl oxalofluoroacetate with ethyl cyanoacetate in the presence of piperidinium acetate. The product so obtained (I) gave, upon treatment with alcoholic sulphuric acid, directly the desired triethyl α-fluoroacnitate (II).



We have not succeeded in hydrolysing (II) without far-reaching degradation of the molecule. However, the biological properties of (II) as such will be of interest, as the complications inherent in the possible stereochemical forms of fluorocitrate<sup>3</sup> are not to be feared in (II).

*Triethyl γ-cyano-α-fluoroacnitate (I).* A mixture of 21 gm. of diethyl oxalofluoroacetate<sup>4</sup>, 14 gm. of ethyl cyanoacetate, 0.5 ml. of acetic acid and 0.1 ml. of piperidine was heated for 20 hr. at 100° in a vacuum of 35 mm. After 6 and again after 13 hr. of this