

With the exception of the complex with nitrite, the two series are almost identical.

This close parallelism suggests that the structural changes of the reacting complexes, that is, the configuration of the activated complex, are very similar in both cases. For the electrode reaction it has been found<sup>4</sup> that, with the exception of the complex  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$  (Vlček, A. A., unpublished results), the complexes are orientated in such a way that the atomic group X is as distant as possible from the electrode surface. This orientation is also very convenient for the substitution reaction, the heterogroup being accessible for the exchange with other reactants without any bond breaking and rearrangement of the complex.

The proof of substitution reactions catalysed by adsorption at the electrode surface is very important for the interpretation of many observations concerning the influence of anions on the electrochemical behaviour of complexes. The presence of many anions causes a great shift of the reduction wave of some complexes towards positive potentials. This shift may be due to a substitution reaction of the type here described, which, when rapid, causes the reduction of the total amount of the depolarizer to take place at positive potentials.

The experimental details and further discussion will be published elsewhere.

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<sup>1</sup> Adell, B., *Z. anorg. Chem.*, **246**, 303 (1941).

<sup>2</sup> Weber, J., Koutecky, J., and Koryta, J., *Z. Elektrochem.*, **63**, 583 (1959).

<sup>3</sup> Basolo, F., and Pearson, R., "Mechanisms of Inorganic Reactions" (John Wiley and Sons, Inc., 1958).

<sup>4</sup> Vlček, A. A., *Discuss. Farad. Soc.*, **26**, 164 (1958).

### Microwave Spectrum of Fluorine Cyanide

A FRACTION of the product of fluorination of cyanogen, in which fluorine cyanide was detected by infra-red spectroscopy<sup>1</sup>, has now been shown to absorb in the microwave regions of 21,000, 42,000 and 63,000 Mc./s. The absorptions occur in the frequency-ranges expected from the resolved rotational structure of the infra-red band,  $\nu_3$ , centred on  $1,077 \text{ cm}^{-1}$ . Their Stark effects and nuclear quadrupole splittings are those expected for  $J = 0 \rightarrow 1$ ,  $1 \rightarrow 2$  and  $2 \rightarrow 3$  transitions in the linear molecule,  $\text{FC}^{14}\text{N}$ . Spectra due to molecules with one quantum of vibrational energy in the degenerate bending mode ( $\nu_2$ ) have also been measured.

Values so far obtained are the rotational constant,  $B_0 = 10,554.20 \pm 0.01 \text{ Mc./s.}$ ; the coupling constant for  $^{14}\text{N} = -2.67 \pm 0.05 \text{ Mc./s.}$ ; the dipole moment,  $\mu = 1.68 \pm 0.05 \text{ D}$ ; and the centrifugal stretching constant,  $D_J = 0.0053 \pm 0.0003 \text{ Mc./s.}$  The quadrupole coupling suggests a C—N distance slightly more than 1.163 Å. found<sup>2</sup> in  $\text{ClCN}$ : if 1.165 Å. is assumed, the C—F distance is obtained as 1.260 Å. This is the shortest C—F distance known, and implies, in agreement with the low value of the coupling constant, an important contribution of  $^+\text{F}=\text{C}=\text{N}^-$  to the structure.

We are at present attempting to improve the yield and the purity of the sample. It should then be possible to detect other isotopic species in natural

abundance (particularly  $\text{FC}^{15}\text{N}$ ). We hope to be able to detect and resolve other infra-red bands to see if the small discrepancy between the microwave and the infra-red (parallel mode)  $B$ -values extends to infra-red values obtained from perpendicular modes.

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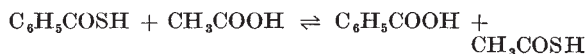
<sup>1</sup> Aynley, E. E., Dodd, R. E., and Little, R., *Proc. Chem. Soc.*, 265 (1959).

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### Thiol Exchange System with Thiolbenzoic Acid

ALTHOUGH many methods for the preparation of thiolacetic acid have been reported<sup>1</sup>, all rely on the use of hydrogen sulphide, preferably under pressure, or phosphorous pentasulphide, which is not pleasant to handle.

It occurred to us that if an equilibrium existed between thiolbenzoic acid and thiolacetic acid:



the reaction might be persuaded to go towards completion by removal of the latter as the lowest-boiling component.

We have, in fact, obtained thiolacetic acid in yields of 95 per cent, based on the thiolbenzoic acid used, by this exchange method which we believe to be novel. Catalytic amounts of water appear to be essential; the most satisfactory method is to reflux glacial acetic acid (2 mol.) under a packed column fitted with reflux head, then gradually (8–12 hr.) add to the still, thiolbenzoic acid (1 mol.) previously saturated by shaking with water. The head temperature falls to 87–89° C. and the thiolacetic acid is withdrawn at such a rate that this temperature is maintained. The product needs drying for storage.

As thiolbenzoic acid is now commercially available the method should be attractive to those wishing to prepare conveniently relatively small quantities of thiolacetic acid.

Thiolpropionic acid was prepared by the same method, but attempts to convert butyl alcohol to butyl mercaptan were unsuccessful.

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<sup>1</sup> "Organic Syntheses", **31**, 108 (1951).

## RADIOCHEMISTRY

### An Alternative Mechanism for Chemical Protection against Radiation Damage

STUDIES of the effects of chemicals in decreasing the radiation damage suffered by exposed organisms have revealed a number of compounds which are quite efficient in this respect<sup>1-3</sup>. While several mechanisms have been suggested for their mode of action<sup>4</sup>, none has been universally accepted. It seems possible that the protective action may function