acid and formates reproduced in Fig. 1 indicate distinctly the correctness of the above assumption, namely, that formic acid is *normal* in constitution, that is to say, the -CH- oscillation  $(2,963 \text{ cm.}^{-1})$  exists in its aqueous solution (Fig. 1, *a*) while in formate solution it is non-existent (Fig. 1, *b*).





We have also examined the infra-red absorption curve for a number of formates (barium, cadmium, sodium, etc.) in the *solid* state. Fig. 2 indicates the infra-red absorption curve of sodium formate in the solid state and also in aqueous solution. The absorption maximum corresponding to  $3.46 \mu$ , characteristic of all aliphatic -CH- linkage, is present in the solid formate but absent from its aqueous solution.



Hence we conclude that formic acid, formic ester

and solid formates are *normal* in structure; abnormality appears in the aqueous solution of formates due to prototropy.

Comparison of  $CO_3''$  and  $NO_3'$  ions reveals the fact that they are isosteric and iso-structural but not iso-electric, carbon being a tetrad and nitrogen a pentad.

$$\begin{bmatrix} \Pi & O \\ N & O \end{bmatrix}' ( \begin{array}{c} \text{Nitrite} \\ \text{ion} \end{array} \text{ and } \begin{bmatrix} \Pi & O \\ C & OH \end{bmatrix}' ( \begin{array}{c} \text{formate ion in} \\ \text{aqueous solution} \end{array} )$$

are isosteric as well as iso-electric, nitrogen being a triad and carbon a diad.

The formate ion in aqueous solution should be logically called 'carbonite', from analogy with nitrite.

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University College of Science, 92 Upper Circular Road, Calcutta. Dec. 12. <sup>1</sup> NATURE, 133, 646 (1934). <sup>2</sup> Bull. Soc. Chim., 51, 57 (1932).

Absorption Spectra of Nitrates in the Vapour State

THE experiments of Franck and his collaborators<sup>1</sup> on the absorption spectra of alkali and silver halides made it desirable to extend such investigations to more complex inorganic molecules. Nitrates appear to be highly suitable for this purpose, since they invariably liberate NO2 as a product of decomposition on heating, which can be easily recognised by its two characteristic sets of bands. Furthermore, the nitrate ion exhibits selective absorption with a sharp maximum at about 300-290 mµ, as shown by alkali nitrates in solution and by solutions of dilute aqueous nitric acid. On the other hand, in nitric acid in the vapour state and in hexane solutions, and also in ethyl nitrate in the vapour state, this maximum disappears and is replaced by a very diffuse and flat one between about<sup>2</sup> 270 mµ and 260 mµ. This evidently gives a simple criterion for the existence of electrovalent and covalent forms.

The absorption spectra of a number of inorganic nitrates have been measured by heating in vacuum, to about 100° above the melting point of the anhydrous salt, in a porcelain tube of 80 cm. length placed in an electric stove and closed by water-cooled quartz windows. Some, such as cadmium nitrate, decompose too rapidly for measurement, but most of the compounds exhibit a flat and diffuse maximum of selective absorption between about 270 mµ and 260 mµ. The figures in mµ are as follows : KNO<sub>3</sub>, 267; AgNO<sub>3</sub>, 263; Mg(NO<sub>3</sub>)<sub>2</sub>, 270; Pb(NO<sub>3</sub>)<sub>2</sub>, 268.

It is therefore concluded that the nitrates are covalently bound in the vapour state and constitute another example of the facile transition from covalent to electrovalent linkage. The absorption spectra of some nitrites and sulphates indicate a similar phenomenon.

A detailed report will be given in the Proceedings of the Indian Academy of Sciences (Bangalore).

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<sup>1</sup> Z. Phys., 43, 155 (1927); 56, 548 (1929); 69, 724 (1931), etc. <sup>\*</sup> Cf., for example, V. Halban and Eisenbrand, Z. phys. Chem. 132, 433 (1928). J. W. Goodeve, Trans. Farad. Soc., 30, 504 (1934).

## Kinetics of Formation and Decomposition of Dicyclo-Pentadiene

THE reaction cyclopentadiene + cyclopentadiene dicyclopentadiene is reversible, and is bimolecular in the direct and monomolecular in the reverse directions. No observation indicates that a chain mechanism is involved. The association was measured in benzene solution between  $15^{\circ}$  and  $55^{\circ}$ , and the