passage of hydrogen through the solution. After precipitation, the ferrous hydroxide and supernatant liquid were left in a flask connected to a manometer, so that any evolution of hydrogen might be detected by a pressure increase. No hydrogen evolution was detected under these conditions, even with ferrous chloride in excess.

Further experiments were then performed, following more closely those of Schikorr<sup>1</sup>. Here the ferrous hydroxide was prepared by precipitation from a ferrous sulphate solution with sodium hydroxide. Under these conditions Schikorr reported evolution of hydrogen at room temperature, when ferrous sulphate was in excess, but not when alkali was in excess. However, in our experiments, no evolution of hydrogen was observed even when the reactants were heated to 100° C.

It was nevertheless found that hydrogen was evolved at room temperature, in the presence of excess ferrous sulphate, if certain additions were made to the solution before precipitation with alkali. These additions included platinum chloride, colloidal platinum, nickel sulphate, nickel powder and copper powder. A smaller evolution was also produced by the addition of sodium sulphide. It is as yet uncertain whether these metals themselves or their ions in solution are the true catalysts, and no views on the mechanism of the reaction are here offered.

No hydrogen has yet been obtained after the addition of manganese sulphate-a matter of obvious importance in connexion with steel.

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## **Reaction of Cyanogen and Related Compounds with Butadiene**

CYANOGEN and butadiene have been found to react at moderately high temperatures (400°-700° C.), forming as the main product 2-cyanopyridine. It has also been established that this behaviour of cyanogen may be generalized for the simple 1,3-dienes<sup>1,2</sup>.

The present communication presents the results of some calculations and experiments with nitriles of the type R—CN, where R is H,CH<sub>3</sub>,C<sub>6</sub>H<sub>5</sub>, as well as CN. In each case, the free-energy change for the reaction :

$$\begin{array}{ccc} + & \mathbf{C} - R & = & & \\ & \parallel & & \\ & \mathbf{N} & & & \mathbf{N} \end{array} + \mathbf{H}_{2} & (1) \end{array}$$

has been calculated over a range of temperatures in order to obtain information useful as a guide in the experimental investigation. These results are summarized in Table 1. The thermodynamic functions for 2-methylpyridine, 2-cyanopyridine and benzonitrile were calculated statistically, the vibrational

frequencies of these compounds being assigned on a semi-empirical basis involving a consideration of the assignment for pyridine and benzene, and also the frequencies associated with the vibrations of the methyl and cyano groups. The functions for 2-phenylpyridine were estimated by a method of increments from the functions of 2-methylpyridine and benzene.

TABLE 1

Reaction 1 with	Product	$\Delta F$ (kcal.) for the reaction			
R as: H CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CN	Pyridine 2-Methylpyridine 2-Phenylpyridine 2-Cyanopyridine	$\begin{array}{c} T^{\circ} \text{ K. 400} \\ -23 \cdot 9 \\ -18 \cdot 9 \\ -7 \cdot 07 \\ -30 \cdot 1 \end{array}$	$\begin{array}{r} 600 \\ -20.9 \\ -14.5 \\ -5.37 \\ -27.2 \end{array}$	$\begin{array}{r} 800 \\ -17.8 \\ -11.1 \\ -4.05 \\ -25.6 \end{array}$	$ \begin{array}{r} 1000 \\ -14.7 \\ -4.66 \\ -3.05 \\ -20.6 \end{array} $

It is seen that the calculated free-energy change is quite favourable over the temperature range in question in each case; but since these results refer to equilibrium in ideal gaseous systems, a quantitative correlation with the experimental work has not been attempted. In Table 2 the data for three comparable vapour-phase experiments are given. The experiments were carried out at atmospheric pressure in an unpacked quartz reaction vessel, using continuous flow technique. The product in each case was identified by its known physical constants, and the melting point and analysis of the picrate. The yields are calculated on the amount of nitrile converted.

TABLE 2

Reaction $\cdot 1$ with $R$ as :	Product	Temp. °C.	Con- tact time	Mol. ratio RCN/ C.H.	Yield of product
H	Pyridine	$595\pm5^{\circ}$	30 sec.	$1 \cdot 1/1 \cdot 0$	5-6 %
CH <sub>3</sub>	2-Methylpyridine	$599\pm5^{\circ}$	30 ,,	$1 \cdot 7/1 \cdot 0$	5-6 "
C <sub>4</sub> H <sub>5</sub>	2-Phenylpyridine	$591\pm5^{\circ}$	31 ,,	$1 \cdot 7/1 \cdot 0$	12-16 ",

These reactions may be explained as proceeding by a Diels – Alder mechanism in which the  $(-C \equiv N)$ has the role of the dienophilic component of the dienophile :

$$\begin{array}{c} + & \mathbf{C} - R \\ \parallel \\ \mathbf{N} \\ \mathbf{N} \end{array} = \begin{bmatrix} & & \\ & \mathbf{N} \\ & & \mathbf{N} \\ \parallel \\ & & \mathbf{N} \end{bmatrix} = \begin{bmatrix} & & \\ & \mathbf{N} \\ & & \mathbf{N} \\ & & \mathbf{N} \\ & & & \mathbf{N} \end{bmatrix}$$

The intermediate (i) has not been observed among the products, and it would seem that it undergoes spontaneous dehydrogenation at these temperatures to form the thermodynamically more stable pyridinic product (ii).

A fuller account of this work is to be published elsewhere. The investigation is being continued.

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