

7: 8-dimethoxy-4-methylcoumarin, (7) 6-methoxy-4-methylcoumarin and (8) 4-methyl-1: 2-*a*-naphtha-pyrone. All of them underwent oxidation with the insertion of the hydroxyl group in 6-position. Where this position was occupied, either the oxidation did not proceed or some abnormal reaction took place. These methoxy-hydroxy-coumarins could be demethylated smoothly with the formation of the unknown 5: 6-dihydroxy-4-methylcoumarin, 5: 6: 7-trihydroxy-4-methylcoumarin, and 6: 7: 8-trihydroxy-4-methylcoumarin. We have applied this method for the synthesis of the natural coumarins scopoletin, fraxinol and fraxetin. Fuller details will be shortly published elsewhere.

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#### ADSORPTION OF HYDROGEN AT ELEVATED PRESSURES ON A PROMOTED IRON SYNTHETIC AMMONIA CATALYST

A STATIC volumetric method, an improvement on that employed by Frolich and White,<sup>1</sup> has been developed for the measurement of adsorption of gases by solids at elevated pressures. Employing this method, the adsorption of hydrogen has been studied on a Fe — K<sub>2</sub>O — Al<sub>2</sub>O<sub>3</sub> — TiO<sub>2</sub> catalyst at seven temperatures ranging from 50° to 350° C. and at pressures from 15 to 50 atmospheres.

The results obtained indicate two distinct types of activated adsorption of hydrogen in the temperature range studied, one showing a maximum at about 150° and the other at about 300° C. Emmett and Harkness<sup>2</sup> have found two types of activated adsorption of hydrogen on a doubly promoted iron catalyst, Type A occurring fairly rapidly between -78° and 0° C. and Type B at 100° C. Presuming that, in conformity with this observation, the present catalyst can also give rise to Type A adsorption and that the maximum found at 150° C. corresponds to the Type B chemisorption, the maximum at 300° C. noted in the present investigation therefore points to the occurrence of a third type of activated adsorption which may be designated as Type C. The occurrence of three different types of activated adsorption of hydrogen on iron can be explained on the basis of the 3-fold

disposition of the iron atoms in the (111) crystallographic plane of the body centred cubic lattice of  $\alpha$ -iron (Fig. 1 of Ref. 3).

The surface area of the catalyst as found by applying the B.E.T. equation<sup>4</sup> to the adsorption of argon on the reduced catalyst at liquid air temperature was 1.85 sq. m. ( $V_m = 0.48$  cc.) per g. of unreduced catalyst. Assuming that in this determination the argon atoms were adsorbed only on the plane of the outermost iron atoms, while in the activated adsorption of hydrogen every iron atom of the surface, in any of the three possible dispositions, could chemisorb a hydrogen atom, an estimate could be made of the maximum adsorption of hydrogen on the part of the surface consisting of free iron atoms, which according to Brunauer and Emmett<sup>3</sup> cover roughly 40 per cent. of the total surface of a doubly promoted catalyst. The results show that beyond about 100° C., the adsorption exceeds the calculated surface saturation limit (0.4 cc./g.) at fairly high pressures. This indicates that especially at the higher pressures, there is marked absorption into the metal lattice. Further proof of the superposition of absorption on chemisorption is provided by the rather low values obtained for the heat of adsorption. For an adsorption of 0.2 cc./g. a value of 4,746 calories per mole is obtained for the heat of adsorption as against 8,500 calories per mole obtained by Emmett and Harkness.<sup>2</sup>

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#### FORMATION AND NEW METHODS OF PREPARATION OF 3-ACETYL-4-CAR- BOXYLIC HEPTANOL-4-DIONE-2-5 CARBOXYLIC MONOETHYL ESTER-1

IN the study of hydroxy and ethoxy methylene derivatives of substituted pyruvic ester, an attempt was made to prepare ethoxymethylene acetyl pyruvic ester (I) by Claisen's orthoformic ester and acetic anhydride method.<sup>1</sup> After removing acetic anhydride, the residual