

**620.** *Investigation of Chemisorption by Radiochemical Techniques. Part V.\* The Adsorption and Hydrogenation of [<sup>14</sup>C]Crotonic and [<sup>14</sup>C]Vinylacetic Acid on Thiophen-poisoned Palladium.*

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It has been shown by means of scintillation counting that <sup>14</sup>C-labelled crotonic and vinylacetic acid are adsorbed from toluene on palladium-barium sulphate. The extent of adsorption was not affected by the presence of a catalyst poison, thiophen, although hydrogenation rates were markedly diminished. It is concluded that only a small fraction of the adsorbed molecules take part in the catalytic hydrogenation and that the catalyst surface is heterogeneous.

ONE of the basic requirements for an understanding of the mechanisms and rates of surface-catalysed processes is a knowledge of which species is being adsorbed during the process and in what amount. In gas-phase reactions pressure changes may be measured fairly easily: in liquid-phase reactions adsorption can be more difficult to follow. However, if the sorbed molecules are radioactive, then their detection and estimation are easier, especially if the detecting device is a liquid scintillation counter. By this radiochemical technique we have now studied the extent of adsorption of crotonic and vinylacetic acid (but-3-enoic acid) on a catalyst surface, in the absence and in the presence of poison, and the degree of uniformity of a catalyst surface.

#### EXPERIMENTAL

<sup>14</sup>C-Labelled Vinylacetic<sup>1</sup> and Crotonic Acid.<sup>2</sup>—Potassium [<sup>14</sup>C]cyanide (0.1 mc in 10 g.) was converted into, successively, cuprous cyanide, allyl cyanide, and vinylacetic acid. This acid was purified by dissolution in alkali. The solution was extracted with ether, then acidified, and the product recovered by further ether-extraction and distilled (b. p. 69–70°/12 mm.).

Some of the vinylacetic acid was then isomerised to crotonic acid by potassium hydroxide solution. The product was recrystallised from water as the *trans*-form, m. p. 71–72°. The radiochemical purity of the materials was satisfactory, for the specific activities of the vinylacetic and the crotonic acid were 1722 and 1682 c.p.m. per mg.

*Toluene.*<sup>3</sup>—Sulphur was removed from the toluene by two distillations over aluminium chloride. The toluene was then washed with water, dried (K<sub>2</sub>CO<sub>3</sub>), and stored over sodium wire.

*Hydrogenation.*—After each hydrogenation the reaction flask was freed from contamination by refluxing toluene and aluminium chloride in it for 30 min.

Hydrogenations were performed in a microhydrogenation apparatus in which the rate of reaction was measured from plots of the volume of hydrogen taken up against time. Several hydrogenations were performed at 20° and a hydrogen pressure of 1 atm. Initial rates were plotted against mg. of poison for both acids in Fig. 1, and against mg. of acid for crotonic acid in the presence and absence of thiophen (Fig. 2).

*Adsorption.*—Adsorptions were carried out from 1.5 ml. of solution by a standardised procedure. A known amount (<1.5 ml.) of pure toluene was added to a centrifuge tube containing 50 mg. of 5% palladium-barium sulphate. This mixture was then pretreated with hydrogen for 1 min. The volume of liquid was then made up to 1.5 ml. by addition of a solution of the radioactive acid in toluene. When adsorptions were studied in the presence of catalyst poison, 0.48 mg. of thiophen was added in toluene, before pretreatment with hydrogen, to the pure toluene in contact with the catalyst. The acid was stirred in contact with the catalyst for 10 min. in a thermostat-bath at 20°. During the next 1½ min. the catalyst was centrifuged

\* Part IV, *Trans. Faraday Soc.*, 1962, **58**, 1170.

<sup>1</sup> *Org. Synth.*, Coll. Vol. I, 2nd edn., 1946, p. 46; Coll. Vol. III, 1st edn., 1955, p. 851.

<sup>2</sup> Goldberg and Linstead, *J.*, 1928, 2343.

<sup>3</sup> Zetzsche and Arnd, *Helv. Chim. Acta*, 1926, **9**, 173.

off. An aliquot part of the supernatant liquid was then transferred to 10 ml. of a liquid scintillator, N.E.213, in a silvered cell 7 by 2.8 cm. The cell was coupled optically by means of silicone oil 704 to the window of a photomultiplier tube, E.M.I. 6097 S, which was cooled by circulating tap-water (13°). The EHT was supplied by a stabilised power pack, Dynatron N.E.103. Pulses from the photomultiplier were fed into a cathode follower and linear amplifier, Dynatron 1430A, single-channel pulse analyser, Dynatron N.101, and rate-meter, Ekco N.522C, and counted on a scaler, Ekco N.529C.

After each adsorption count had been taken, a standard scintillation cell was counted to check the performance of the equipment. All counts were taken to 1% statistical accuracy. It was found, by counting a C-14 source and then adding inactive acid, that the quenching brought about by crotonic acid was 3.1% per mg., and by vinylacetic acid was 2.5% per mg. As for thiophen, even if this is as strong a quencher as an aldehyde, 0.2 mg. will quench to an extent less than 1%. The effect of varying the equilibration time was also studied for both acids. Equilibrium was attained after 1 min. in both cases.

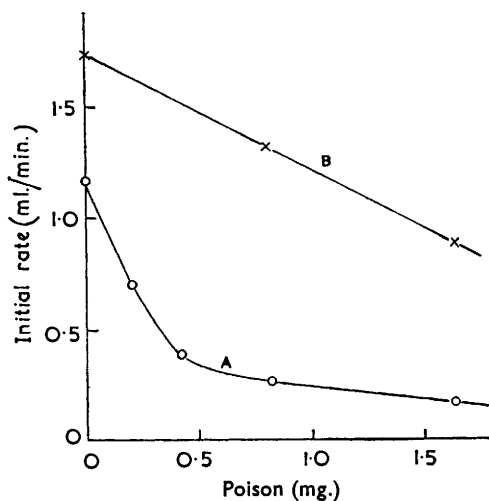


FIG. 1

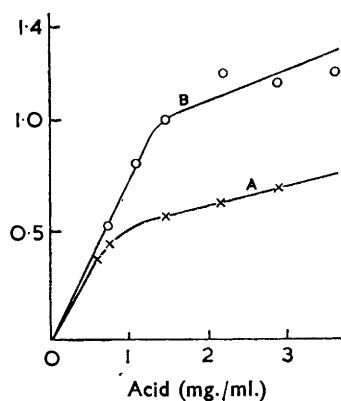


FIG. 2

FIG. 1. Thiophen-poisoning curves for (A) crotonic and (B) vinylacetic acid in toluene at 20°. Initial rates of hydrogenation are plotted against amount of poison. 50 mg. of 5% Pd-BaSO<sub>4</sub>; total vol. 5 ml. Crotonic acid 14.1 mg., vinylacetic acid 13.6.

FIG. 2. Hydrogenation-rate curves for crotonic acid in toluene at 20°. Initial rates are plotted against amount of crotonic acid in (A) presence and (B) absence of thiophen. 50 mg. of 5% Pd-BaSO<sub>4</sub>, total vol. 5 ml.

## RESULTS AND DISCUSSION

The results (Fig. 1) show that thiophen is an effective catalyst poison in the hydrogenation of vinylacetic acid (but-3-enoic acid) and is particularly effective in inhibiting hydrogenation of crotonic acid, where a flexed linear type of poisoning curve results.<sup>4</sup>

It appears from the adsorption results shown in Fig. 3 that both acids are adsorbed on the catalysts and that the presence or absence of poison makes no detectable difference to the adsorption. Thus the simple explanation of the mode of operation of a poison, that poison keeps the reactants off the catalyst surface, is not tenable in this example.

The most likely picture of the hydrogenation process uses Herington and Rideal's

<sup>4</sup> Maxted, *Adv. Catalysis*, 1951, **3**, 129.

model,<sup>5</sup> as follows. Crotonic acid is adsorbed extensively on the surface, but not all the sorption sites are involved in catalysis. Instead, only a small fraction take part. Herington and Rideal's model then gives the proper shape of the poisoning curve.

If these catalytic sites are progressively poisoned then adsorption of crotonic acid on those sites will be diminished and so rate of reaction will decrease. This diminution in adsorption is masked by the much more extensive general adsorption.

In the case of vinylacetic acid the flexed linear type of poisoning curve was not obtained at the concentrations used. However, a substantial poisoning effect due to thiophen was

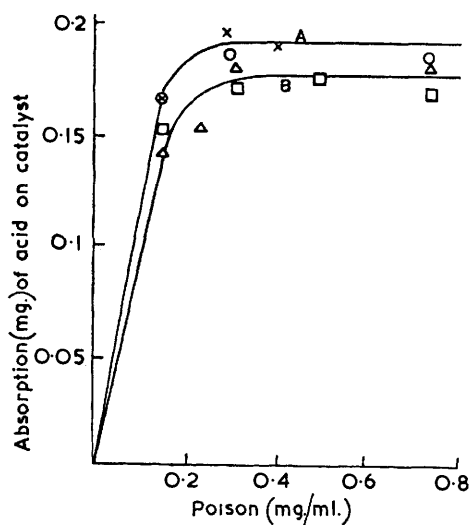


FIG. 3. Adsorption of (B) [<sup>14</sup>C]crotonic and (A) [<sup>14</sup>C]vinylacetic acid in toluene (5 ml.) on 5% Pd-BaSO<sub>4</sub> in presence (×, Δ) and absence (O, □) of thiophen (0.48 mg.).

noted. But again no corresponding decrease in extent of adsorption could be demonstrated (Fig. 3).

Further evidence for the postulate of hydrogenation on a limited number of sites comes from a study of Figs. 2 and 3. There it can be seen that extensive adsorption of crotonic acid takes place, yet the curves for hydrogenation rate against concentration flatten when only 1—2 mg. of crotonic acid are present. This suggests saturation of a small number of hydrogenation sites in the early stages of adsorption.

Thus it seems that there is no simple relation between adsorption and catalysis and that not all the adsorption sites are involved in catalysis.

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<sup>5</sup> Herington and Rideal, *Trans. Faraday Soc.*, 1944, **40**, 505.