861. *Synthetical Applications of Activated Metal Catalysts. Part XI.* A Comparative Study of the Toxic Effects of Pyridine and 2,2'-Bipyridyl on Some Raney Catalysts.*

By G. M. Badger, G. D. F. Jackson, and W. H. F. Sasse.

The rate of hydrogenation of *trans*-crotonic acid in the absence and in the presence of pyridine and 2,2'-bipyridyl has been measured with five Raney nickel catalysts and one Raney cobalt catalyst. Except for the last all catalysts are poisoned by these bases. Pyridine is more toxic than 2,2'-bipyridyl towards W-1 and W-2 Raney nickel, and the opposite has been found with W-6 and W-7 nickel. The W7-J catalyst is equally poisoned by both bases. Pyrrole poisons W-7 nickel more than W7-J catalyst.

The formation of 2,2'-biaryls from pyridine and related bases under the influence of a degassed Raney nickel catalyst has been described earlier in this series.[1] The results obtained so far indicate that this reaction occurs while the reactants are adsorbed on the catalyst, presumably *via* the lone electron pairs of the nitrogen atoms. The outcome of the reaction should therefore depend *inter alia* on the adsorption–desorption equilibria of the reactants and products. Maxted and Walker [2] have shown that the catalytic toxicity of pyridine depends on the availability of the lone electron pair for adsorption on the catalyst, and it was thought that more insight into the adsorption processes occurring during the formation of 2,2'-bipyridyl from pyridine might be gained by an examination of the catalytic toxicity of pyridine and 2,2'-bipyridyl. We now report results of a preliminary study of the influence of these bases on the rate of hydrogenation of *trans*-crotonic acid in the presence of W-1,[3], W-2,[4] W-6,[5] W-7,[5] and W7-J [6] Raney nickel as well as of a Raney cobalt catalyst.[7] As traces of pyrrole are formed in the reaction between pyridine and W7-J nickel the effect of this compound on the activity of W-7 and W7-J nickel was also examined.

EXPERIMENTAL

Materials.—Methanol was distilled from sodium hydroxide through the column described earlier [8] (reflux ratio 1 : 5), and the fraction of b. p. 64·5° (n_D^{21} 1·32859) was used. Pyridine was fractionated from potassium hydroxide (reflux ratio 1 : 10) and the fraction of b. p. 115—115·5° (n_D^{21} 1·5020) was used. *trans*-Crotonic acid (m. p. 72°) was obtained by recrystallisation from light petroleum. 2,2'-Bipyridyl (m. p. 71·5—72°) was purified by chromatography on alumina and crystallised from light petroleum. Synthetic pyrrole was distilled under nitrogen and in the absence of light. A fraction, b. p. 131°, was used immediately. W-1,[3] W-2,[4] W-6,[5] W-7,[5] and W7-J [6] nickel catalysts were prepared from 50 : 50 aluminium–nickel alloy (B.D.H.). The cobalt catalyst [7] was prepared from 70 : 30 aluminium–cobalt alloy (Light's).

Hydrogenations.—The hydrogenations were carried out in a Towers microhydrogenator at atmospheric pressure in methanol (volume of mixture made up to 10 c.c.) while the flasks were being shaken at 315 ± 35 vibrations per min. All hydrogenations involving one catalyst were carried out with portions of the same preparation of catalyst at the temperature indicated in Table 1. Poisons (0·000012 mole) were added and equilibrated (50—60 min.) with the catalyst before crotonic acid (0·0104 g.) was introduced. After completion of a run the catalyst was filtered off and weighed.

Method of Comparison.—The rate of hydrogenation of crotonic acid was measured in each

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* Part X, *J.*, 1960, 2969.

[1] Badger and Sasse, *J.*, 1956, 616.

[2] Maxted and Walker, *J.*, 1948, 1093.

[3] Covert and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 4116.

[4] Mozingo, *Org. Synth.*, 1941, **21**, 15.

[5] Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695.

[6] Sasse, *J.*, 1959, 3046.

[7] Aller, *J. Appl. Chem.*, 1957, **1**, 130.

[8] Badger, Rodda ,and Sasse, *J.*, 1954, 4162.

TABLE 1. *Hydrogenations of crotonic acid.*

Weight of catalyst (g.)	Initial rate (c.c./min.)	Poison [a]	Weight of catalyst (g.)	Initial rate (c.c./min.)	Poison	Weight of catalyst (g.)	Initial rate (c.c./min.)	Poison
W-1 *Nickel*, 22°			W-6 *Nickel*, 20°			W7-J *Nickel*, 20°		
0·0960	1·09	—	0·0359	1·14	—	0·0346	0·44	—
0·0368	0·45	—	0·0281	1·00	—	0·0276	0·34	—
0·0865	0·94	—	0·0324	0·99	—	0·1170	1·36	—
0·0121	0·13	—	0·0150	0·48	—	0·0780	0·86	—
0·0147	0·04	Pyridine	0·0290	0·60	Pyridine	0·0809	0·38	Pyridine
0·0422	0·13	,,	0·0882	2·20	,,	0·0414	0·17	,,
0·0420	0·11	,,	0·0318	0·66	,,	0·0613	0·25	,,
0·0530	0·15	,,	0·0190	0·45	,,	0·0700	0·27	,,
0·0669	0·22	2,2′-Bipyridyl	0·0710	1·37	2,2′-Bipyridyl	0·0900	0·37	2,2′-Bipyridyl
0·0570	0·20	,,	0·0188	0·35	,,	0·0395	0·16	,,
0·0640	0·20	,,	0·0602	1·08	,,	0·0789	0·37	,,
0·0239	0·07	,,	0·0340	0·62	,,	0·0770	0·34	,,
						0·0302	0·21	Pyrrole
W-2 *Nickel*, 18°			W-7 *Nickel*, 19°			0·0630	0·42	,,
0·0437	0·91	—	0·0252	0·83	—	0·1115	0·66	,,
0·0164	0·42	—	0·0062	0·12	—	0·0272	0·22	,,
0·0298	0·65	—	0·0604	1·85	—			
0·0818	1·70	—	0·0501	1·80	—	*Cobalt*, 18°		
0·0732	0·32	Pyridine	0·0527	1·34	Pyridine	0·0115	0·05	—
0·0339	0·13	,,	0·0344	0·88	,,	0·0144	0·05	—
0·0843	0·42	,,	0·0160	0·30	,,	0·0188	0·11	—
0·0510	0·15	,,	0·0584	1·63	,,	0·0471	0·36	—
0·0739	0·57	2,2′-Bipyridyl	0·0409	0·43	2,2′-Bipyridyl	0·0318	0·29	—
0·0397	0·33	,,	0·0350	0·45	,,	0·0078	0·01	Pyridine
0·0203	0·17	,,	0·0187	0·28	,,	0·0334	0·27	,, [b]
0·0423	0·33	,,	0·0787	1·22	,,	0·0116	0·10	,, [c]
			0·1143	1·79	Pyrrole	0·0258	0·15	,, [a]
			0·0268	0·45	,,	0·0205	0·06	,, [d]
			0·0240	0·39	,,			
			0·0364	0·55	,,			

[a] 0·000012 mole, [b] 0·00000063 mole, [c] 0·0000012 mole, [d] 0·00012 mole, each in 10 c.c. of mixture.

FIG. 1. *The relation between the rate of hydrogenation of crotonic acid and the weight of* W-2 *Raney nickel catalyst*: (*A*) *in the absence of poison*; (*B*) *in the presence of* 2,2′-*bipyridyl*; (*C*) *in the presence of pyridine.*

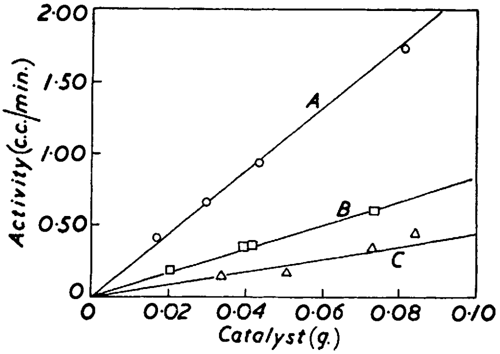
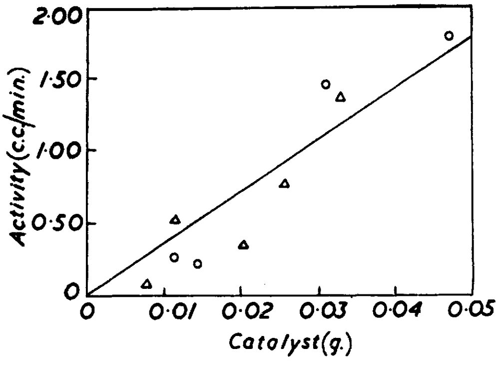


FIG. 2. *The relation between the rate of hydrogenation of crotonic acid and the weight of Raney cobalt catalyst*: ○, *in the absence of poison*; △ *in the presence of various concentrations of pyridine.*



run by the slope of the hydrogenation curve at its origin. As the weight of a Raney catalyst cannot be determined accurately until completion of a run, a series of experiments was carried out in which the weight of catalyst was varied (0·01—0·1 g.) while the other variables were kept constant. In this way linear relations between the rate of hydrogenation and the weight of catalyst were obtained. Repetition of these experiments in the presence of each poison (0·000012 mole) gave other linear relations of lower slope (Fig. 1).

From these graphs the activity of 0·05 g. of each catalyst (poisoned and unpoisoned) was read off (Table 2); these values were then expressed as poisoning coefficients which are known to be unaltered by small temperature changes.[9] The Raney cobalt catalyst lost its activity so rapidly that freshly prepared samples had to be used for each run. This may account for the relatively large deviations from a linear relation between rate of hydrogenation and weight of catalyst observed with this preparation. Within the accuracy of this graph, pyridine did not alter the activity of this catalyst (Fig. 2).

TABLE 2.

Catalyst (temp.)	Activity of unpoisoned catalyst	Activity in presence of pyridine	Activity in presence of 2,2′-bipyridyl	Activity in presence of pyrrole
W-1 Ni (22°)	0·56	0·14	0·16	—
W-2 Ni (18°)	1·08	0·20	0·40	—
W-6 Ni (20°)	1·64	1·20	0·94	—
W-7 Ni (19°)	1·64	1·30	0·68	0·78
W7-J Ni (20°)	0·60	0·21	0·21	0·33
Co (18°)	(0·36)	(0·36)	—	—

Reaction between Pyridine and W-1 *Nickel.*—Pyridine (150 c.c.) was refluxed over W-1 nickel[3] (prepared from 125 g. of alloy) for 50 hr. The mixture was worked up as previously described,[1] to give 2,2′-bipyridyl (19·5 g.) and complex (2·5 g.).

DISCUSSION

The activities of the unpoisoned nickel catalysts in the hydrogenation of *trans*-crotonic acid (Table 2) are in the expected order as the activity of Raney nickel catalysts for hydrogenations is known to increase with the amount of hydrogen left on the nickel during its preparation.[10] Partial removal[11] of this hydrogen at a later stage results in a linear decrease of catalytic activity and reduction of the surface area.[12] This effect is seen in the loss of activity of the W-7 catalyst during the preparation of W7-J nickel (which involves heating *in vacuo* at 100°).

The low activity of the Raney cobalt catalyst resembles its low efficiency in desulphurisation.[13] This catalyst is not detectably affected by pyridine (see above) and this may be related to its failure to bring about the formation of 2,2′-bipyridyl from pyridine.[14]

The lowering of the activities of all nickel catalysts by pyridine and 2,2′-bipyridyl (Table 3) corroborates Maxted and Walker's findings;[2] and in agreement with other observations,[15] the most active preparations are affected least by these bases. Pyrrole, however, poisons the hydrogen-rich W-7 catalyst more than the W7-J nickel, but it is likely that the poisoning coefficient measured with W-7 nickel is that of a more basic hydrogenation product of pyrrole, namely, pyrrolidine.[16]

TABLE 3. *Poisoning coefficients* ($\times 10^{-4}$).

Catalyst	Pyridine	2,2′-Bipyridyl	Catalyst	Pyridine	2,2′-Bipyridyl	Pyrrole
W-1	6·3	6·0	W-7	1·7	4·9	4·2
W-2	6·8	5·3	W7-J	5·4	5·4	2·7
W-6	2·2	3·6				

The less active nickel catalysts are more susceptible to poisoning by pyridine than by 2,2′-bipyridyl while the opposite holds for W-6 and W-7 nickel. This reversal of the toxicities of pyridine and 2,2′-bipyridyl suggests that adsorption of 2,2′-bipyridyl on the more active catalysts is also followed by further changes leading to compounds which are more toxic than pyridine. Preliminary experiments have shown that 2,2′-bipyridyl reacts

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[9] Maxted and Stone, *J.*, 1934, 26; Maxted, *Adv. Catalysis*, 1951, **3**, 167.
[10] Adkins and Krsek, *J. Amer. Chem. Soc.*, 1948, **70**, 412.
[11] Kokes and Emmett, quoted by Emmett, *J. Phys. Chem.*, 1959, **63**, 449.
[12] Smith, Chadwell, and Kirslis, *J. Phys. Chem.*, 1955, **59**, 820.
[13] Badger, Kowanko, and Sasse, *J.*, 1959, 440.
[14] Sasse and Whittle, unpublished work.
[15] For references see Maxted, *Adv. Catalysis*, 1951, **3**, 166.
[16] Devereux, Payne, and Peeling, *J.*, 1957, 2845.

with W-7 nickel to give pyrrole derivatives [17] and such a change could account for the increase in catalytic toxicity of 2,2′-bipyridyl observed with the W-6 and W-7 catalysts.

It is not known whether the relative magnitude of the poisoning coefficients of pyridine and 2,2′-bipyridyl as now determined constitutes one of the factors determining the efficiency of a catalyst in the preparation of 2,2′-bipyridyl from pyridine, but it is noteworthy that the W7-J catalyst, which is equally poisoned by both bases, is a better catalyst in this reaction than W-7 nickel [6] or the W-1 catalyst.

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UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, May* 16*th*, 1960.]

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[17] Sasse, unpublished work.