

SHORT COMMUNICATIONS

RANEY NICKEL CATALYSED HYDROGEN-EXCHANGE REACTIONS*

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Nickel on kieselguhr is a selective catalyst for the exchange with deuterium oxide of hydrogen in a variety of aromatic and alkylaromatic compounds.^{1,2} In the present investigation degassed Raney nickel similar to that used for the synthesis of bipyridyl³ and in other reactions^{4,5} was compared with nickel on kieselguhr in respect of its ability to catalyse the exchange with deuterium oxide of the hydrogen of benzene, ethylbenzene, *p*-cresol, *p*-methylanisole, pyridine, and quinoline.

The environments in which the most readily exchanged hydrogen atoms were found were almost identical for the two catalysts. Thus, with both catalysts benzylic hydrogen, the methyl hydrogen of ethylbenzene, hydrogen *ortho* to the hydroxyl of *p*-cresol (but not hydrogen *ortho* to the methoxyl of *p*-methylanisole), hydrogen *ortho* to the amino group of aniline, and the 2- and 6-hydrogens of pyridine, exchanged readily; while the aromatic hydrogen of benzene and ethylbenzene, H 3 and H 5 of *p*-cresol and aniline, and H 3, H 4, and H 5 of pyridine exchanged more slowly. The results with degassed Raney nickel are presented in Tables 1 and 2.‡ This catalyst proved to be less selective than nickel on kieselguhr; for example, in runs in which the alkyl hydrogen of ethylbenzene had exchanged to similar extents there was more exchange of the aromatic hydrogen over the Raney nickel. With quinoline there was—in addition to the facile exchange of H 2, H 7, and H 8 found over nickel on kieselguhr—substantial exchange of H 3 and slight exchange of other hydrogen. Thus in its ability to catalyse exchange of aromatic hydrogen the degassed Raney nickel appears to be intermediate between nickel on kieselguhr, which has little activity except for aromatic hydrogen in particular environments,¹ and such catalysts as palladium on charcoal;⁶ palladium black, platinum black, and nickel on alumina;⁷ and reduced platinum oxide,⁸ which catalyse the exchange with deuterium oxide of aromatic hydrogen of ethylbenzene or *p*-xylene at a rate at least comparable with that of the benzylic hydrogen.

* Manuscript received September 24, 1965.

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‡ For comparison, results of an exchange of *p*-methylanisole over nickel on kieselguhr are included in the table. They will be fully discussed elsewhere.

¹ Macdonald, C. G., and Shannon, J. S., *Tetrahedron Lett.*, 1964, 3351.

² Macdonald, C. G., and Shannon, J. S., *Aust. J. Chem.*, 1965, **18**, 1009.

³ Sasse, W. H. F., and Whittle, C. P., *J. Chem. Soc.*, 1961, 1347.

⁴ Sasse, W. H. F., *J. Chem. Soc.*, 1960, 526.

⁵ Jackson, G. D. F., and Sasse, W. H. F., *Aust. J. Chem.*, 1964, **17**, 337.

⁶ Macdonald, C. G., and Shannon, J. S., *Tetrahedron Lett.*, 1963, 1349.

⁷ Hirota, K., and Ueda, T., *Bull. Chem. Soc. Japan*, 1962, **35**, 228.

⁸ Garnett, J. L., and Sollich-Baumgartner, W. A., *J. Phys. Chem.*, 1965, **69**, 1850.

The p.m.r. assignments were straightforward except those for quinoline, which are shown in Figure 1. An AB quartet (J 8.3 c/s) is assigned to ^1H 3 and ^1H 4 of those molecules where both are present. There is partial collapse of the downfield part of this quartet to a singlet, broadened by *ortho* coupling to deuterium,

TABLE 1
RESULTS OBTAINED WITH RANEY NICKEL CATALYST

Substrate	Reaction Time (hr)	Average Number of D Atoms* per Molecule in	Whole Molecule
Benzene	264		3.83
Ethylbenzene	3.0	methyl, 1.60, 3; methylene, 1.23, 2; ring, 0.19, 5	3.02
Ethylbenzene	24.0	methyl, 2.68, 3; methylene, 1.86, 2; ring, 0.46, 5	5.01
<i>p</i> -Cresol	4.0	methyl, 2.63, 3; H 2+H 6, 1.74, 2; H 3+H 5, 0.58, 2	4.95
<i>p</i> -Methylanisole†	91	benzylic, 2.86, 3; methoxyl, -0.04, 3; ring, 0.05, 4	2.87
Aniline	24.0	H 2+H 4+H 6, 1.96, 3; H 3+H 5, 0.57, 2	2.53
Pyridine	3.0	H 2+H 6, 1.63, 2; H 3+H 5, 0.06, 2; H 4, 0.03, 1	1.72
Quinoline	24.0	H 2, 0.94, 1; H 3, 0.68, 1; H 4, 0.10, 1; H 8, 0.95, 1; H 5+H 6+H 7, 1.06, 3‡	3.74

* Results are listed in the order: group, average number of D atoms, total number of hydrogen ($^1\text{H}+\text{D}$) atoms in the group.

† Exchange using nickel on kieselguhr catalyst as previously described.²

‡ H 5 and H 6 are little, and H 7 almost completely exchanged.

which is due to ^1H 4 of molecules in which ^1H 3 has been replaced by deuterium. The rest of the signals closely approximate an AB quartet (J 8.3 c/s) and are therefore due to two only of the remaining protons ^1H 5, ^1H 6, and ^1H 7.

TABLE 2
RELATIVE ABUNDANCE OF DEUTERIUM-SUBSTITUTED MOLECULES

Substrate	Number of D Atoms per Molecule								
	0	1	2	3	4	5	6	7	8
Benzene	0.065	0.091	0.101	0.121	0.162	0.230	0.230	—	—
Ethylbenzene	0.031	0.121	0.226	0.253	0.216	0.108	0.029	0.012	0.002
Ethylbenzene	—	—	0.003	0.037	0.217	0.552	0.102	0.061	0.028
<i>p</i> -Cresol	—	0.005	0.013	0.059	0.224	0.403	0.244	0.052	—
<i>p</i> -Methylanisole	0.004	0.118	0.878	—	—	—	—	—	—
Aniline	0.003	0.081	0.466	0.309	0.124	0.018	—	—	—
Pyridine	0.032	0.309	0.567	0.090	0.002	—	—	—	—
Quinoline	—	—	0.053	0.309	0.504	0.123	0.012	—	—

Black and Heffernan⁹ found, for neat quinoline, $J_{5,6}$ 8.15 c/s, $J_{5,7}$ 1.60 c/s, and $J_{6,7}$ 6.81 c/s; so that the magnitude of the coupling constant of the remaining AB quartet indicates that it is due to ^1H 5 and ^1H 6, while ^1H 7 is largely replaced

⁹ Black, P. J., and Heffernan, M. L., *Aust. J. Chem.*, 1964, 17, 558.

by deuterium. Assignment of the upfield part of the quartet to $^1\text{H}6$ and the downfield to $^1\text{H}5$, as required by the analysis of Black and Heffernan, is confirmed by the relative broadness, due to *ortho* coupling to deuterium, of the upfield part of the quartet.

The close similarity in behaviour of the two catalysts suggests that the same exchange mechanisms are involved, at least for the hydrogen which is most readily exchanged.

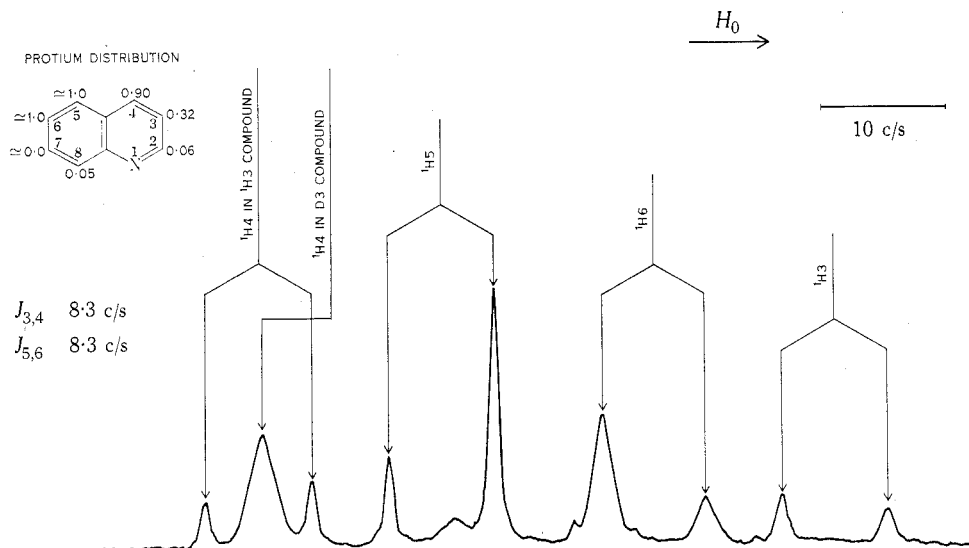


Fig. 1.—Portion of p.m.r. spectrum of partly deuterated quinoline. (Signals due to residual $^1\text{H}2$ and $^1\text{H}8$ occurred farther downfield and are not shown.)

Experimental

For each reaction a borosilicate glass reaction tube as previously described,² containing 1:1 aluminium–nickel alloy (B.D.H., 50 mg) and 28% w/v sodium hydroxide solution (0.5 ml), was gently agitated for 30 min in a bath maintained at 50–52°. The catalyst was then washed at ambient temperature by passing water (150 ml) slowly through a long capillary which reached to the bottom of the reaction tube. The washings were then neutral to litmus. The bulk of the wash water remaining in the reaction tube was removed by pipette, the remainder was frozen, and the tube was connected to a pump maintaining a pressure of 0.2–0.3 torr. When the ice had evaporated the temperature was raised to 100° for 30 min. The system was allowed to cool and nitrogen was then admitted to atmospheric pressure, followed by deuterium oxide (99.8 atom % D, 2.0 ml) and the substrate (0.3 ml). The tube was cooled in liquid nitrogen, evacuated to 0.2–0.3 torr, and sealed.

The exchange reaction (with agitation at 45–50 r.p.m.) and subsequent working up, and the mass-spectral and p.m.r. examination of the product, were carried out as previously described² except that best separation of the p.m.r. resonances of quinoline was obtained with the neat material, which allowed estimation of $^1\text{H}2$, $^1\text{H}3$, $^1\text{H}4$, $^1\text{H}8$, and $^1\text{H}5 + ^1\text{H}6 + ^1\text{H}7$. Diluting the quinoline with carbon tetrachloride caused the $^1\text{H}8$ and $^1\text{H}4$ resonances to merge.

Acknowledgments

The authors thank Dr W. H. F. Sasse and Dr J. S. Shannon for their interest in the work.