Technical Papers

Selective Reduction of the Unsaturated Compounds: Deuterization of the Raney Nickel Catalysts

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Experience with deuteration and hydrogenation of the unsaturated compounds (*1, 2*) has indicated that both processes are of the same nature and follow the same pattern of reactions. Apparently the catalysts reduce the differences in reaction characteristics of the two isotopes. As a result of these observations, it was deemed desirable to prepare deuterized Raney nickel for deuteration of the unsaturated compounds. In the present investigation, only those hydrogenation catalysts which are prepared free of alkali were used. The traditional catalysts, W-1 (*3*), W-2 (*4*), and W-3 (*5*) satisfy this requirement. Of these three, W-1 is the least active and therefore can be used for reduction of unsaturation without reduction of the ester group, but W-2 and W-3 are equally active in both cases. For these reasons, W-1 was used for reducing methyl stearolate to di-deutero-oleate and W-2 and W-3 were allowed to reduce 9, octadecyne to 9, 10-di-deutero-octadecene in order to determine the extent of deuteration. However, these catalysts may be employed for all types of deuteration, in the same manner as for hydrogenation (*3–7*).

For deuterization, the catalysts were stored in purified dioxane (*8*). Twenty-five g of Raney nickel (still wet with dioxane) were twice washed with 25 ml portions of dioxane by centrifugation. The catalyst was then transferred to a 250-cc modified reaction vessel (Fig. 1) of the Joshel hydrogenator (*9*) by washing it into the vessel with 50 ml of dioxane. Stopcock *a* just above the reaction vessel was closed, the main system evacuated, flushed with D_2 gas and then the reservoir of the apparatus was filled with 300 ml D_2 gas. Stopcocks *b* and *c* were opened and oxygen-free nitrogen was allowed to flush the reaction vessel. On closing stopcock *b* a sufficient vacuum was applied through stopcock *c* by means of a water pump to draw out the nitrogen gas with a minimum vaporization of the dioxane. Stopcock *c* was then closed and *a* was opened. The reaction vessel was filled with D_2 gas under a slight pressure, as indicated by difference in mercury level of 2.5 cm in the manometer of the hydrogenator. Stopcock *a* was closed, and the catalyst was agitated in the presence of D_2 gas for 3 hr. The reaction vessel was again flushed with oxygen-free nitrogen, and the above process was repeated five times. Then the vessel was again flushed, filled with fresh D_2 gas, and the catalyst was agitated for 24 hr. Nickel prepared in this manner was stored in brown bottles, filled with dioxane through which D_2 had been bubbled and to which a few ml of D_2O had been added. These stored materials should be completely protected from oxygen, ordinary water, halogen, and sulfur compounds. Since W-2 and W-3 catalysts hold more hydrogen (*7*), it was necessary to agitate the catalyst for 3 hr in each of seven changes of D_2 before the final 24-hr exposure. The deuterium analyses of the deutero compounds prepared by the different catalysts were very satisfactory, being in the range of 95–98 atoms per cent.

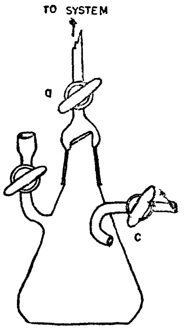

FIG. 1. Reaction vessel for deuterization.

Future plans include investigation to determine the best ways to deuterize the alkaline catalysts, W-4 (*5, 10*), W-5 (*11*), and W-7 (*11*), as well as the alkali-free catalyst W-6 (*11*), which contains the greatest amount of hydrogen. Deuterium content of the gases held by the individual catalysts will be investigated by mass spectrographic analysis. The preparation of these deuterized catalysts will facilitate deuteration and deuterolysis of organic compounds that may be used as "tracers" in both the chemical and biological reactions.

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Manuscript received July 7, 1952.

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[2] The author wishes to thank F. E. Deatherage and J. B. Brown, of Ohio State University, for their help during the progress of the work.