

and that physically adsorbed molecules possess mobility in the plane of the surface.

Details will follow shortly.

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HAZARDS IN CATALYTIC HYDROGENATION AT ELEVATED TEMPERATURES AND PRESSURES

Sir:

T. S. Carswell [THIS JOURNAL, 53, 2417 (1931)] has reported an explosion which occurred while he was attempting to hydrogenate *o*-nitroanisole in the liquid phase with a nickel catalyst. He states that the purpose of his communication "is to call the attention of other investigators to the dangers of this type of reduction when carried out on other than a very small scale." There is no doubt that a warning is needed but in my opinion it should be against the procedure used by him and not against catalytic hydrogenation at elevated temperatures and pressures. This general method has been in successful use in this Laboratory for the past three years [THIS JOURNAL, 52, 4349, 5192 (1930); 53, 1091, 1095, 1402, 1425, 1868, 2012 (1931); *J. Phys. Chem.*, 35, 1684 (1931)] using a wide variety of compounds and dealing with quantities similar to those used by Dr. Carswell. The procedure used by him is, in my opinion, ill-advised in several respects. The bomb was inadequate and sufficient information was not available to him before the attempt was made to hydrogenate 400 g. of nitroanisole. A bomb for experimental purposes 15 cm. in diameter should have a wall thickness several times as great as that (5 mm.) used by Carswell. Our own bombs have a wall thickness of 2 to 2.5 cm. and are only 6 cm. in internal diameter. They were bored out of properly annealed rolls of nickel-chromium steel [*cf.* Ernst, *Ind. Eng. Chem.*, 18, 664 (1926)]. In order to control the rate of hydrogenation it is important that the bomb be provided with a thermometer or thermocouple well, so designed that there is little lag between the actual temperature of the liquid contents of the bomb and the reading of the temperature measuring device.

The temperature and amount of catalyst used by Carswell were excessively high for the compound to be hydrogenated, and apparently he made no attempt to control the rate of hydrogenation by control of the rate of shaking of the bomb. The reactions are quite exothermic and would result in local superheating if heat was being liberated more rapidly than it could be dissipated. In the hydrogenation of 100 g. of toluene with less than 0.5 g. of nickel, for example, we have observed a temperature rise of as much

as 150° within two or three minutes. In the hydrogenation of only 20 g. of nitrophenol at 100° with 0.3 g. of nickel a temperature rise of 100° was observed. It is not surprising that in the hydrogenation at 250° of 400 g. of nitroanisole in the presence of perhaps 50 g. of nickel, the temperature of the contents of the bomb rose so high that there resulted an explosive decomposition.

There is little doubt that after suitable investigation the catalytic hydrogenation of such compounds as nitroanisole can be carried out on a commercial scale in relatively light equipment. However, one is not justified, as Carswell has demonstrated, in attempting to hydrogenate even so small a quantity as a few hundred grams of material without preliminary study and without having available a properly designed bomb.

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POSITIVE ION CATALYSIS IN THE KNOEVENAGEL REACTION

Sir:

Dakin [*J. Biol. Chem.*, **7**, 49 (1909)] found that amino acids might be employed in place of the amines usually used to effect condensations of the Knoevenagel type. In the presence of amino acids, the velocity of the condensation of cinnamic aldehyde with malonic acid in 50% alcohol was found to increase with increase in the hydrogen-ion concentration of the solution [D. L. Klein, Master's Thesis, New York University, 1930]. This result suggested the amino acid cation to be a more active catalyst than the other ions derivable from the ampholyte. As is well known, secondary aliphatic amines are preferable to primary amines for the catalysis of reactions of this type. Since, as a rule, such secondary amines are stronger bases than the corresponding primary amines, it appeared that with such substances the amine ion is the active catalyst. In agreement with this concept various amines have been found to be more active catalysts in acid solutions.

Extremely weak bases such as urea do not ordinarily appear to catalyze condensations of the Knoevenagel type in aqueous or alcoholic solution. When, however, the solutions are made strongly acid, such weak bases display some catalytic activity. By taking advantage of the fact that weak bases dissolved in acetic acid appear to be highly dissociated, it was found that in this solvent urea and similar substances are extremely efficacious catalysts for the condensation of aldehydes with substances containing an "active" methylene group.

On the basis of these results, it is concluded that condensations of the