

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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RECEIVED JUNE 20, 1931  
PUBLISHED JULY 8, 1931

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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

Knoevenagel type are instances of positive ion catalysis. The details of this investigation will shortly be submitted to THIS JOURNAL.

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RECEIVED JUNE 18, 1931  
PUBLISHED JULY 8, 1931

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### THE SEPARATION OF COLUMBIUM AND TANTALUM

*Sir:*

When columbium is reduced in acid solution from a valence of five to a valence of three the solution becomes blue. In the course of a study of the electrolytic reduction of columbium, with a view to the separation of this element from tantalum, reduction in alkaline solution was attempted. Although no color change was obtained, the formation of an amalgam at the mercury cathode was noted. This suggested the possibility of obtaining metallic columbium in the form of an amalgam by reduction in alkaline solution. Shortly thereafter the writer's attention was called to the article of Fink and Jones,<sup>1</sup> where they show that tungsten can be plated from a saturated solution of sodium carbonate at elevated temperature and high current density. Since that time, the writer has found that, at a current density of approximately 3 amp./sq. dm. and a temperature of 103°, columbium may be plated from a saturated solution of sodium carbonate containing ignited columbium oxide ( $Cb_2O_5$ ). A copper cathode was used. Tantalum will not plate out from a similar bath under identical conditions of temperature and current density. Further, it has been found that a metallic plate is obtained from a carbonate bath containing a mixture of the ignited oxides of columbium and tantalum using the same temperature and current density as that indicated above. It seems to be a fairly safe conclusion that only columbium may be plated from a saturated solution of sodium carbonate containing a mixture of the ignited oxides of tantalum and columbium.

At present further studies are being made concerning the nature of the plates obtained by this method.

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RECEIVED JUNE 20, 1931  
PUBLISHED JULY 8, 1931

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<sup>1</sup> C. G. Fink and F. L. Jones, *Trans. Am. Electrochem. Soc.*, Preprint 59-27, 273 (1931).