THE PREPARATION OF EUROPIUM(II) PROPYNIDE

Edward Murphy and Gerald E. Toogood Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada.

(Received 5 April 1971)

We report the preparation of eruopium(II) propynide, $Eu(CH_3C=C)_2$, by reaction of propyne on a solution of europium in liquid ammonia at -78°C. The material, which is pyrophoric, hydrolyses under controlled conditions to yield propyne and europium(II) hydroxide.

Attempts to prepare the corresponding ytterbium(II) propynide have not been completely successful. The product contains essentially equimolar amounts of the propynide and of ytterbium(II) amide, $Yb(NH_2)_2$.

Experimental

Reagents

Europium and ytterbium metals (99.9% pure) were obtained from American Potash and Chemical Corporation. The europium was in the form of a small ingot which was stored under oil to prevent oxidation; ytterbium was obtained as metal turnings which appeared insensitive to oxidation.

Ammonia and propyne were Matheson research grade. Ammonia was dried over sodium before use but was otherwise not further purified. Propyne was contaminated with acetylene and dimethylacetylene (gas chromatographic evidence) to the extent of about 1% of the former and 3% of the latter.

755

EUROPIUM(II) PROPYNIDE

Theoretically the dimethylacetylene should be inert and this was found to be true in a separate experiment so no great effort was made to remove it in subsequent runs. However, acetylene was considered undesirable as it was known to react with the metal/ammonia solutions. Propyne was freed of acetylene by fractional distillation at -112°C, at which temperature propyne is essentially non volatile whereas acetylene has a vapour pressure of 75 mm Hg.

Method

A weighed amount of metal (ca. 1 mmole) was added to a reaction flask in a dry-box. The flask was equipped with an inlet tube for passage of propyne and an outlet for removal of propyne, ammonia and other volatile materials. The inlet tube reached to near the bottom of the flask so that the propyne could pass into the liquid ammonia solution. A glass-covered stirring bar was also included. (Teflon coated bars seemed to react with the solutions as they were stained black irreversibly after only a few minutes in contact with the solution.)

Dry ammonia was distilled into the reaction flask using conventional vacuum line techniques. The contents of the flask were warmed to -78°C, using a dry-ice/acetone bath, and the resulting metal/ammonia solutions were dark blue-black or bronze depending on the amount of metal dissolved, The maximum concentration achievable was approximately 1 mmole per 150 ml of liquid ammonia.

Propyne was allowed to enter the solution slowly under a pressure differential obtained by introducing the gas at almost atmospheric pressure into a portion of the line adjacent to the reaction flask. Upon opening the flask to the line the propyne passed into the flask as the pressure therein was considerably less than atmospheric. The gas appeared to be extremely soluble in liquid ammonia in which fact it resembles acetylene (1,2).

In the case of europium the colour of the solution changed from blue

756

EUROPIUM(II) PROPYNIDE

to green to yellow as the passage of propyne was continued. Eventually a yellow-brown precipitate formed within the solution. This was recovered by removing the ammonia by pumping (a filtration at -78°C indicated that the liquid contained no soluble material and thereafter filtration was not used as it was a more difficult procedure). The final product, after all ammonia had been removed, was a brown solid.

An analogous set of observations was made with ytterbium. However, the colour changes within the solution were blue - to wine red followed by the precipitation of a mauve-red material.

Analysis

The compounds were analysed for metal content by dissolving the materials in concentrated nitric acid and evaporating the solutions several times to dryness prior to the standard EDTA volumetric analyses (5). Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratory, New York.

Hydrolyses were performed using water vapour generated in vacuo by gently heating copper sulphate $(CuSO_4.5H_2O)$. The gaseous products were examined by infrared spectroscopic, mass spectrometric, and gas chromatographic techniques.

Results

Europium(II) propynide was produced in the procedure described, as indicated by the analytical data (Eu Found 65.9% Theoretical 66.08%; C Found 31.6% Theoretical 31.3%; H Found 2.8% Theoretical 2.61%). The hydrolysis products were propyne and europium(II) hydroxide. In the case of the ytterbium reactions the product appeared to be a mixture of propynide and amide as evidenced by the hydrolysis data which showed that essentially equal

757

amounts of ammonia and propyne were released. The elemental analyses are consistent with this idea (Yb found 78%, Yb($CH_3C=C$)₂ requires 68.9%, Yb(NH_2)₂ requires 84.3%. An equimolar mixture of amide and propynide would contain 76% Yb).

Discussion

The production of europium(II) propynide as outlined above appears to follow an analogous pathway to that invoked for europium(II) acetylide (1,2) in a similar experiment. Thus we may write

1. Eu + liquid ammonia \longrightarrow Eu²⁺ + 2e⁻ 2. 2e⁻ + 2CH₃C=CH \longrightarrow 2CH₃C=C⁻ + H₂+ 3. Eu²⁺ + 2CH₃C=C⁻ \longrightarrow Eu(CH₃C=C)₂+

The corresponding product when acetylene is used is the acid acetylide $Eu(HC \equiv C)_2$, which can be converted to the acetylide, EuC_2 , by deacetylenation at 90°C under vacuum. This final step cannot take place in the case of propyne since there is only one acidic hydrogen.

The propynide as prepared above did not contain ammonia except in trace amounts. This is in agreement with our work on europium acetylide. (In contrast, Anderson and co-workers prepared EuC_2 1.5NH₃ by a similar reaction using acetylene (3).)

Hydrolysis products of carbides are notoriously variable unless the conditions are mild and consistent (3,6,7). This seems especially true when acetylene is a potential product. However, we found that europium propynide could be reacted consistently with water vapour to yield propyne as the sole carbon-containing species. Europium(II) hydroxide was the companion product. Very slight traces of ammonia were obtained and these could either have come from adsorbed gas on the propynide or, more likely, from traces of amide produced by the reaction 4, since europium ammonia solutions are unstable with 4. $Eu^{2+} + 2e^{-} + 2NH_3 \longrightarrow Eu(NH_2)_2^+ + H_2^+$

respect to the reaction, albeit slowly relative to the reaction with propyne or acetylene. In favour of this latter proposal are our observations on ytterbium reactions, as solutions of ytterbium in liquid ammonia are far less stable than those of europium.

An interesting observation of reactions involving liquid ammonia solutions of europium and ytterbium is the intensities of the colours of the products. The europium materials tend to be bright yellow or orange-red and those of ytterbium are dark red to brown (1,2,3,4).

References

- 1. H.D. FRAME, Argonne National Laboratory, private communication.
- 2. E. MURPHY, M.Sc. Thesis, University of Waterloo, 1970.
- 3. J.S. ANDERSON, J. Inorg. and Nucl. Chem. 30, 105 (1968).
- 4. L.L. PYTLEWSKI and J.K. HOWELL, Chem. Comm. 1280 (1967).
- 5. R. BANE and P. PETERSON, Argonne National Laboratory, private communication.
- H.J. SVEC, J. CAPELLEN and F.E. SAALFELD, J. Inorg. Nucl. Chem. 26, 721 (1964).
- 7. G.J. PALENIK, Ph.D. Thesis, University of Southern California (1959).