Tetrahedron Letters,Vol.26,No.50,pp 6245-6248,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

OLIGOMERISATION OF PHENYL ACETYLENE OVER TITANIUM OXIDE SUPPORTED ON SILICA - ALUMINA CATALYST

V.G. Kumar, T.S. Shoba
Polymers and Special Chemicals Division
Vikram Sarabhai Space Centre, Trivandrum - 695022, India

and
K.V.C. Rao
Chemicals Group
Vikram Sarabhai Space Centre, Trivandrum - 695022, India

Abstract: Titanium oxide on silica-alumina support is found to be effective for oligomerisation of phenyl acetylene. Cyclic trimerisation of the acetylene leading to trisubstituted benzene was also found to occur during the oligomerisation, in addition to the formation of small quantities of a ketone by the reaction of phenyl acetylene with moisture over the catalyst surface.

Transition metal complexes, usually with Lewis acid cocatalysts are generally reported to be employed for polymerisation and oligomerisation of Alkynes, along with many other catalysts. [1-5] of these, tungsten and molybdenum based catalysts[6,7] are shown recently to be the most effective ones. At present, there is tremendous research interest in the polymerisation of acetylenic monomers or oligomers into high purity acetylenic polymers to be doped to deliver conducting polymers. Heterogeneous catalyst systems when employed for polymerization could improve the purity and there exists scant literature on the oligomerisation/polymerisation of alkynes on these types of catalysts. The mechanistic studies on the aromatic alkylation[8] and olefin oligomerisation reactions[9-11] catalysed by surface supported transition metal oxide catalysts developed in our laboratory indicated the possibility of employing supported transition metal oxide catalysts for alkyne polymerisation. Thus, titanium oxide on silica alumina support was found to oligomerize phenyl acetylene along with minor quantities of side products like acetophenone and triphenyl benzene.

The catalyst was prepared as per the procedure described elsewhere[8]. The reactions were carried out by the dropwise introduction of phenylacetylene into a cylindrical glass reactor of 1" diameter packed with catalyst beads. The temperature of the reaction was maintained at 220°C and the product was collected continuously at the bottom of the reactor. The product hold up in the reactor was extracted by passing toluene immediately after the last drop of the reactant was fed in. The toluene was further removed by vacuum distillation. 5 gms of phenylacetylene gave rise to a product mixture of 4.5 gms, which still contained some unreacted precursor. The unreacted precursor was further removed by vacuum distillation, which amounted to 0.8 gms. Figure 1 compares the IR spectrum of pure phenylacetylene (Fig.1A) with that of the product obtained after complete removal of unreacted phenylacetylene (Fig.1.B). Presence of carbonyl group (1690 cm^{-1}), olefinic unsaturation (1650 cm^{-1}), shift in the acetylenic absorption to 2250 cm^{-1} due to conjugation,[12] specific cis-substitution bonds (740,895,1370 cm^{-1}) and trans substitution bonds (920,970,1265 cm^{-1})[13] are indicated by the IR Spectrum 1 B.

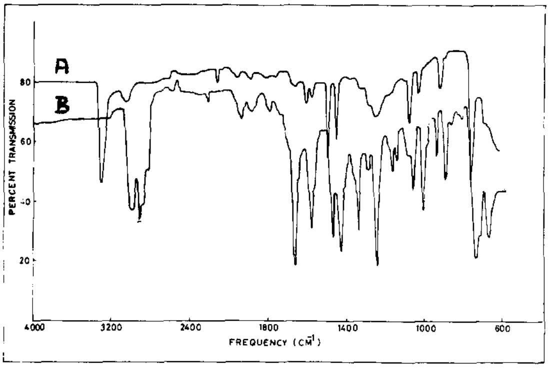


Figure 1: IR spectrum of phenylacetylene prior to (1A) and after (1B) the oligomerisation reaction over titanium oxide on silica alumina catalyst.

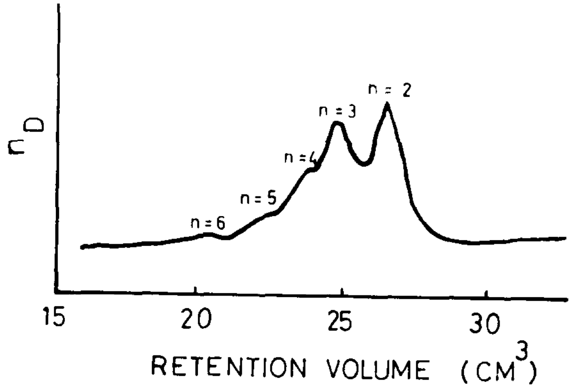


Figure 2: GPC of the oligomer of phenylacetylene when passed over titanium oxide on silica alumina catalyst.

The product was fractionated with methanol, where the pale yellow coloured solid fraction which was insoluble in methanol (3.0 gm, fraction I) and the methanol soluble portion (0.7 gm, fraction II) were characterised separately. The IR spectrum of I did not indicate any carbonyl absorption at 1690 cm^{-1}, but indicated conjugated double bonds at 1640 cm^{-1}, in addition to a weak absorption at 2250 cm^{-1}, for C≡C. The H'NMR spectrum of fraction I gave a broad absorption between 7.04 and 7.90δ. This and the absence of any other peak in the NMR indicate the possible presence of only aromatic and conjugated protons in the sample. The GPC of this fraction (Fig.2) shows the sample to be a mixture of five components having retention volumes corresponding to molecular weights around 200,300,400,500 and 600 as per the calibrations to the particular GPC conditions. Phenylacetylene precursor has a molecular weight of 102 and the GPC suggests the fraction I to be a mixture of its oligomers and is confirmed by the mass spectrum as shown in Fig.3. Molecular ions of the oligomer of more than trace occurance (dimer, trimer and tetramer) in the GPC have given rise to well defined peaks at m/e 204,306,408 in the mass spectrum. In addition, these molecular ion peaks were associated with $(M + 2)^+$ peaks at 206,308 and 410 which are suggested to be due to hydrogenated products of the corresponding oligomer. Similar transition metal oxide supported catalyst is known to promote partial hydrogenation under comparable conditions[9,10].

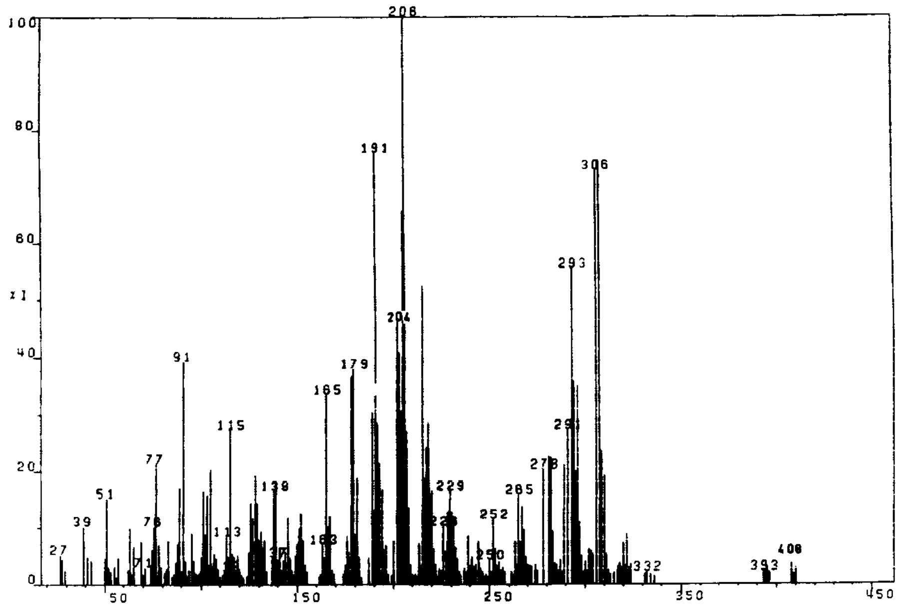


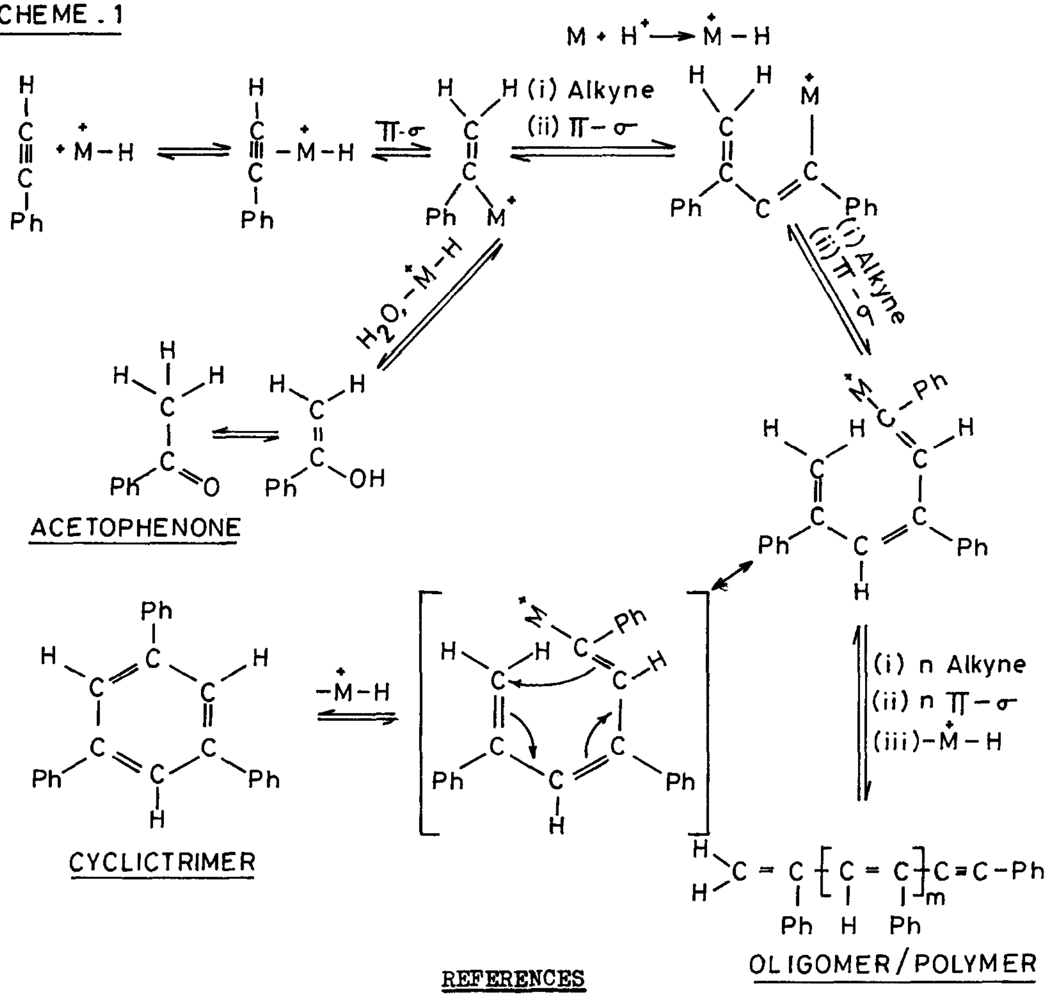
Figure 3 : Mass spectrum of the oligomer of phenylacetylene (methanol insoluble fraction) when passed over titanium oxide on silica alumina catalyst.

Our previous experimental results over this and similar catalysts on alkylation of aromatics and olefinic oligomerisation supported by the mechanistic ideas of these reactions$^{8-11}$ over the catalyst is made use of in suggesting a plausible mechanism for the acetylene oligomerisation. The catalyst was shown to possess protonated transition metal ($\overset{+}{M}$-H) centres which π complexes with the olefin or aromatic compound and involves in a π-σ rearrangement further, to lead to the respective products, at times after repetition of the steps with fresh reactants. Similarly, the oligomerisation of acetylenes over the same catalyst could be expected to involve identical steps and thus, the formation of oligomers is suggested to take place as per scheme I.

This scheme also indicates the possibility of cyclic trimerisation of the acetylene to lead to tri-substituted benzene, and the formation of ketone, which probably involves the residual water present in the catalyst. These products are in fact identified in the IR Spectrum of the methanol soluble portion (fraction II). The NMR spectrum indicated a sharp singlet at 2.6 δ and a multiplet between 7.0 and 7.9 δ. The mass spectra of this shows peaks of m/e 120 and 306 which are attributed to acetophenone and the cyclic trimer (Scheme I). This is in agreement with the NMR chemical shifts, although the integrations could not be matched, due to the product being a mixture.

Efforts are put in to strike conditions favouring the ketone conversion alone over the catalyst and to improve the yield of the oligomerisation by suitable modifications & activation of the catalyst.

SCHEME . 1



REFERENCES

1) Martin B.Jones, Peter Kovacic, Douglas Lanska., J.Polym.Sci;Chem.Ed., 19 (1), 89, (1981)
2) James S.Hwang and Christon P. Tsonis., Polymer, 22, 1462 (1981)
3) R.J. Kern, J.Polym.Sci: Part A-1, 7, 621 (1969)
4) Christon P. Tsonis and Michael F. Farona., J.Polym.Sci: Polym.Chem.Ed., 17, 1779 (1979)
5) Franzus B, Canterino P.J, Wickliffe R.A., J.Am.Chem.Soc., 81, 1514(1959)
6) Toshio Masuda, Toshiyuki Ohtori, Toshinobu Higashimura., Polym.Prepr.,Am. Chem.Soc., Div. Polym.Chem. 20 (1), 731 (1979)
7) Toshio Masuda, Kan-i-chi. Hasegawa and Toshinobu Higashimura., Macromolecules - 7, 728 (1974)
8) V.G. Kumar, T.S. Shoba and K.V.C. Rao., Tetrahedron Letters., 26(27), 3281 (1985)
9) V.G. Kumar, M. Rama Rao, P.V. Ravindran and K.V.C. Rao., J.Polym.Sci : Polym.Chem.Ed., 21, 2133 (1983)
10) V.G. Kumar, S. Venkatachalam & K.V.C. Rao J.Polym.Sci: Polym.Chem.Ed., 22, 2317 (1984)
11) S. Venkatachalam, V.G. Kumar and K.V.C. Rao., J.Polym.Sci : Polym. Chem.Ed., 22, 3805 (1984)
12) Norman B. Colthup, Lawrence H. Daly and Stephen E. Wiberly.,Introduction to Infrared and Raman Spectroscopy, Academic, New York,2nd ed, 1975
13) I. Simionescu, V. Percec, Svetlana Dumitrescu.,J.Polym.Sci: Polym.Chem. Ed., 15, 2497 (1977)

(Received in UK 15 October 1985)