

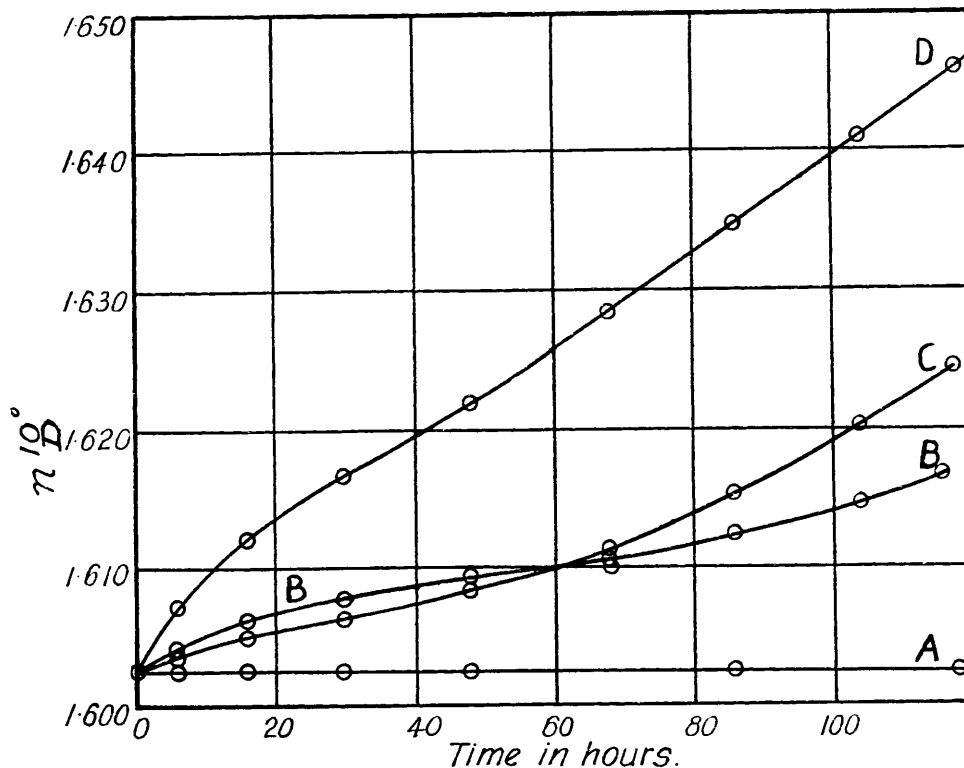
184. The Synthesis and Properties of 2-Iodo-1-vinylacetylene.

By THOMAS H. VAUGHN and J. A. NIEUWLAND.

MONOSUBSTITUTED acetylenes are iodinated by iodine in liquid ammonia (Vaughn and Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 2150), and 2-iodo-1-vinylacetylene is thus obtainable from vinylacetylene at -34° in an almost theoretical yield. In this respect vinylacetylene differs from the alkylacetylenes, which require higher temperatures and give a low yield of the iodoacetylene, and resembles more closely the arylacetylenes.

Preparation.—To iodine (100 g.), dissolved in liquid ammonia (1.7 l.), vinylacetylene (35 g.) was added and after 20 hours the ammonia was boiled off over a water-bath until the residual

FIG. 1.



A, -34° ; B, 25° ; C, 40° , stabilised with 1% quinol; D, 40° , unstabilised.

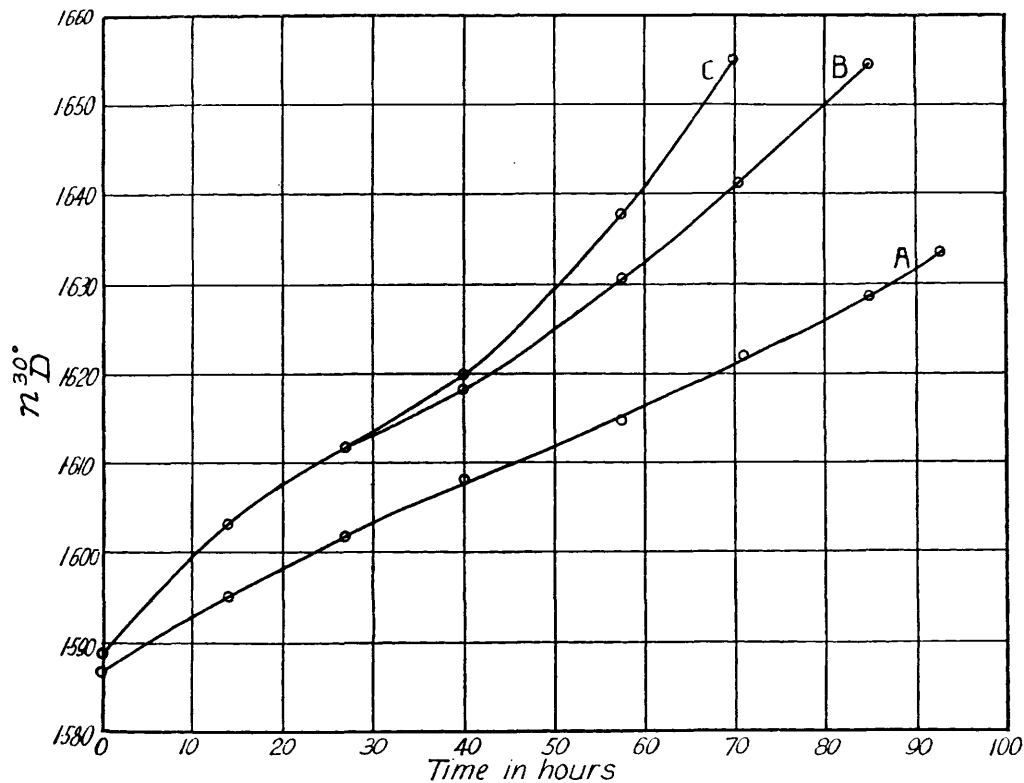
volume was about 250 c.c. Water (1 l.) was slowly added in a fine stream and the heavy oil which separated was washed with water, dried over calcium chloride at 0° , and distilled, giving 67.0 g. (96% of the theoretical amount) of material, b. p. $71.5-71.6^{\circ}/102$ mm. (Found: I, 71.2. Calc. for C_4H_3I : I, 71.35%).

The freshly prepared, pure liquid is colourless and has an extremely unpleasant odour resembling that of di-iodoacetylene. n_D^{25} 1.58904; a_D^{25} 1.8874; $[R_L]_D$ 31.77 (calc., 31.45); γ^{25} 34.62 dynes (maximum bubble pressure method; Sugden, J., 1924, **125**, 27); $[P]$ 230.3 (calc., 230.0, from values given by Mumford and Phillips, J., 1929, 2113). Vapour pressures (mm. \pm 0.3 mm.) $97.5/70^{\circ}$, $115.7/75^{\circ}$, $139.0/80^{\circ}$, $168.0/85^{\circ}$, $201.5/90^{\circ}$; whence, by interpolation, the b. p. at 125 mm. is 77.5° .

In the presence of air 2-iodo-1-vinylacetylene polymerised at room temperature. The colourless liquid turned yellow, then brown, jellied, and finally set to a hard resin-like mass. After 40 days at 40° the material was hard and brittle. Another sample of the same specimen kept at 25° polymerised in the same time to a soft jelly. Still another sample kept at -34° underwent no apparent change.

Oxygen appears to be necessary for the change and is absorbed in large quantities: the rate of polymerisation seems to be a function of its partial pressure. In pure oxygen at 25° the change is very rapid, the gel stage being reached in 10–14 hours. Samples sealed in tubes with air and oxygen darkened and underwent an initial change, but did not solidify even after 7 months. As would be expected, anti-oxidants exert a retarding influence on the change. Samples of iodovinylacetylene stabilised with 1% of quinol, after being kept at 40° for 40 days and then at room temperature for 2 months, had only polymerised to a thick viscous liquid. That this change is polymerisation and not merely oxidation is shown by the enormous increase in the average molecular weight of the material during the change. At 0° this increase was 100% in 10 hours. It is probable that the total change represents both oxidation and polymerisation.

FIG. 2.



A, pure material; B, 1% hydrogen iodide added; C, 1% iodine added. Temp. 42° in all cases.

Iodine and, less effectively, hydrogen iodide and ammonia each accelerate the change. The surface tension of the compound remained constant up to the gel stage, where measurement became difficult, but other physical properties underwent pronounced change during the polymerisation. The density at 30° of a sample kept at 42° in contact with air increased from 1.875 to 2.040 in 89 hours.

The change in the refractive index was used to study the polymerisation. Fig. 1 shows the change of n_D^{30} with time for samples of the material contained in loosely stoppered bottles and thus having limited access to oxygen. A comparison of curve C with curve D clearly shows the retarding action of quinol.

The effect of iodine and hydrogen iodide is brought out in Fig. 2 by plotting n_D^{30} against time for materials kept at 42° in open glass bottles providing a freer contact with oxygen: this condition, together with the slightly higher temperature, accounts for the more rapid change in curve A (Fig. 2) as compared with curve B (Fig. 1).

The hard masses produced by the polymerisation of the unstabilised iodovinylacetylene are sensitive to shock. When struck sharply or rubbed harshly, the polymeride deflagrates, emitting iodine vapour and clouds of heavy brownish smoke. Polymerides in the soft jelly stage are not

inflammable. If a portion of this jelly is washed with ether or alcohol, a light buff-coloured precipitate separates and the unchanged iodovinylacetylene goes into solution. The precipitate is very sensitive to oxygen, darkening rapidly in its presence. The dry precipitate on warming decomposes violently, giving iodine vapour and leaving a swollen mass of carbon. The substance is sensitive to shock in much the same way as the totally polymerised material.

By the same method of washing, polymerides can be isolated in the early stages of the polymerisation. Such material is very light in colour and avidly takes up oxygen. It does not seem to be as combustible as polymerides obtained at a later stage of the change. Polymerides from material stabilised with anti-oxidants are difficultly inflammable, but are quite insensitive to shock.

THE UNIVERSITY, NOTRE DAME, INDIANA.

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