

Liquid VA has a strong tendency to polymerize (16). At higher temperatures and fast heating rates the polymerization will set free enough heat to produce an explosion. The data for the thermal stability of vinylacetylene/butadiene mixtures given in the literature (23 a,e) are very sensitive to the experimental conditions, above all to the heating rate!

It is evident that any mixture of butadiene and vinylacetylene can be considered explosive if temperatures and pressures are high enough and the heat removal from the system is slower than the heat production by a polymerization reaction due to adiabatic storage of the mixture or very fast heating rates. As the VA concentration is increased in the system, lower temperature and pressure are generally required for initiation of explosive decomposition.

The addition of an aqueous solution of sodium nitrate, 12 % (w/w), apparently lowers the explosion temperature of these liquid mixtures; 0.5 % (w/w) solutions show no effect on this temperature limit (23 a,e).

The polymerization of liquid vinylacetylene is accelerated by oxygen. The polymer formed in the presence of air contains peroxides that are self igniting on impact (16).

The relatively low temperatures for beginning self-heating of 1,3-butadiene/vinylacetylene mixtures given by UCC (23 a,e) are valid only in the presence of the liquid phase at very high vapor pressures (> 40 bar). No self-heating due to polymerization could be detected in the gas phase at lower pressures. No self-heating was observed, when the gas mixtures with up to 60 % (mole/mole) VA were stored for 6 h at 130 °C and 10 bar (19). Extensive studies of the self-decomposition of vinylacetylene/1,3-butadiene mixtures in the gas phase have been performed by UCC (23 a,e), the Home Office in Great Britain (20) and BASF (18).