Synthesis of vanadyl acetylacetonate – Protocol M

$$2NH_4VO_3 + 3H_2SO_4 + C_2H_6O + 4(Hacac) + 2Na_2CO_3 \rightarrow 2[VO(acac)_2] + C_2H_4O + (NH_4)_2SO_4 + 2Na_2SO_4 + 6H_2O + 2CO_2$$

Reaction. In a 50 mL beaker, prepare a solution of 2 g (18.9 mmol) of sodium carbonate (about 339% excess) in 15 mL of water. Place 0.5 g (4.3 mmol) of ammonium metavanadate in a 125 mL Erlenmeyer flask. Slowly add 1.5 mL of distilled water, 1 mL (18.4 mmol) of concentrated sulphuric acid (about 185% excess) and 2.5 mL (42,8 mmol) of ethanol (about 1892% excess). Heat for 30 minutes or until the solution turns blue. Cool the solution with running water and add 1.3 mL (12.6 mmol) of acetylacetone (about 47% excess). Slowly add a solution of sodium carbonate and stir with a stirring rod.

Isolation. Filter the solid on a Büchner funnel, wash with plenty of water and with 5 mL of ethanol. Dry in air.

Purification. Not prescribed.

Safety. See hazards associated with the reagents in Table 1.

Greenness Assessment. The evaluation was performed using the Green Star (GS) and the results are shown in Figure 1.

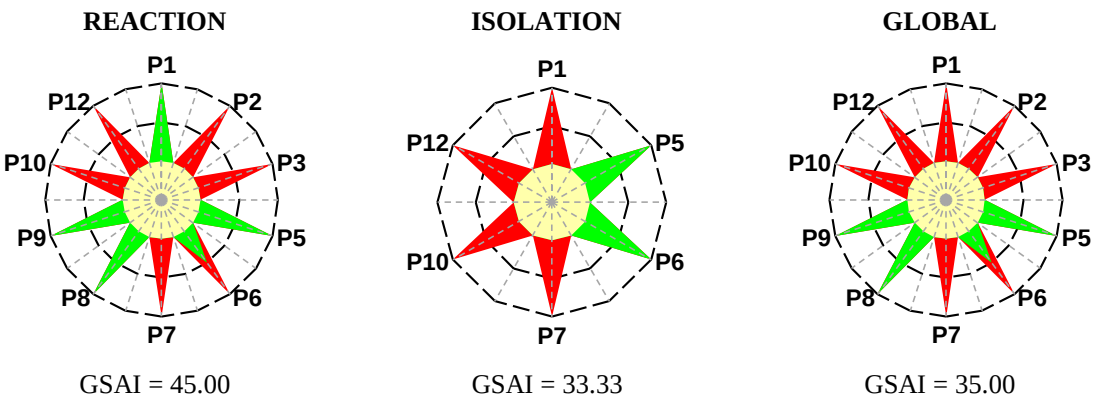

Figure 1. Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate

Construction of the GS

$$2NH_4VO_3 + 3H_2SO_4 + C_2H_6O + 4(Hacac) + 2Na_2CO_3 \rightarrow 2[VO(acac)_2] + C_2H_4O + (NH_4)_2SO_4 + 2Na_2SO_4 + 6H_2O + 2CO_2$$

Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

Table 1. Hazards for the synthesis of vanadyl acetylacetonate, protocol M[α]

Substances involved	Step			Hazard code	Score: hazards to...		
	R	I	Pu		HH	E	P
Stoichiometric reagents							
Acetylacetone[c] (CAS 123-54-6)	✓			H226, H302	2	1	2
Ammonium metavanadate (CAS 7803-55-6)	✓			H301, H315, H319, H330, H335	3	1	1
Ethanol[b] (CAS 64-17-5)	✓			H225	1	1	3
Sodium carbonate (CAS 497-19-8)	✓			H319	2	1	1
Sulphuric acid (CAS 7664-93-9)	✓			H314	3	1	1
Auxiliary substances							
Solvents							
Ethanol (CAS 64-17-5)		✓		H225	1	1	3
Water[a,b]	✓	✓		-	1	1	1
Product							
Vanadyl acetylacetonate (3153-26-2)	✓	✓		H302, H315, H319, H335	2	1	1
Waste							
Acetylacetone[c] (excess)		✓		H226, H302	2	1	2
Ammonium sulphate (aqueous solution)		✓		-	1	1	1
Carbon dioxide	✓			H280	1	1	2
Ethanal		✓		H224, H302, H317, H319, H335, H351	3	1	3
Ethanol[b]		✓		H225	1	1	3
Sodium carbonate (aqueous solution)		✓		-	1	1	1
Sodium sulphate (aqueous solution)		✓		-	1	1	1
Sulphuric acid (dilute solution)		✓		-	1	1	1
Water[a,b]		✓		-	1	1	1

[α] R – Reaction; I – Isolation; Pu – Purification; HH – Human Health; E – Environment; P – Physical
[a] Renewable; [b] Degradable to innocuous products; [c] Degradable

Table 2. Scores used to construct the green star for the synthesis of vanadyl acetylacetonate, protocol M[α]

Green Chemistry Principle	Reaction		Isolation		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	3	Carbon dioxide	1	Ethanal, H351	1	Ethanal, H351
P2 Atom Economy	1	Excess of reagents > 10%, formation of by-products		NA	1	Excess of reagents > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Ammonium metavanadate, H301, H330, sulphuric acid, H314, ethanal, H351		NA	1	Ammonium metavanadate, H301, H330, sulphuric acid, H314, ethanal, H351
P5 Safer solvents and auxiliary substances	3	Water	3	Water and ethanol	3	Water and ethanol
P6 Increase energy efficiency	2	0 ºC ≤ T ≤ 100 ºC	3	Room temperature	2	0 ºC ≤ T ≤ 100 ºC
P7 Use renewable feedstocks	1	Substances not renewable	1	Substances not renewable	1	Substances not renewable
P8 Reduce derivatives	3	One stage		NA	3	One stage
P9 Catalysts	3	Without catalysts		NA	3	Without catalysts
P10 Design for degradation	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable
P12 Safer chemistry for accident prevention	1	Ammonium metavanadate, H301, H330, sulphuric acid, H314, ethanal, H224, ethanol, H225	1	Ethanol, H225, and ethanal, H224	1	Ammonium metavanadate, H301, H330, sulphuric acid, H314, ethanal, H224, ethanol, H225

[α]s – Score; NA – Not applicable

References

Universidade Federal de Viçosa, *https://www2.cead.ufv.br/serieconhecimento/wp-content/uploads/edicao-1.pdf* (accessed January 2012).