Synthesis of vanadyl acetylacetonate – Protocol C

$$V_2O_5 + 2H_2SO_4 + C_2H_6O + 4(Hacac) + 2Na_2CO_3 \rightarrow 2[VO(acac)_2] + 2Na_2SO_4 + C_2H_4O + 5H_2O + 2CO_2$$

Reaction. Place 2.5 mL distilled water in a 25 mL round-bottomed flask and slowly add 2.5 mL (46 mmol) of concentrated sulphuric acid (about 229% excess). Then add 6 mL (103 mmol) of ethanol (about 1395% excess) followed by 1.25 g (7 mmol) vanadium pentoxide. Attach a water cooled condenser and reflux this mixture for about 1.5 hours using a heating mantle. Cool the mixture and filter using a small plug of glass wool, discarding any solid residue. Add 3 mL (29 mmol) of acetylacetone (about 6% excess) dropwise to the filtrate with stirring. Neutralize the mixture by adding it carefully to a solution of 10 g (94 mmol) of anhydrous sodium carbonate (about 586% excess) in 75 mL of distilled water, contained in a 250 mL beaker, while stirring the mixture. Cool the resulting mixture in an ice bath for 15 minutes.

Isolation. Suction filter the resulting mixture. Wash the dark green product with two portions of 5 mL of cold distilled water. Dry under vacuum for 15 minutes, then dry in a vacuum desiccator over anhydrous calcium chloride.

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.

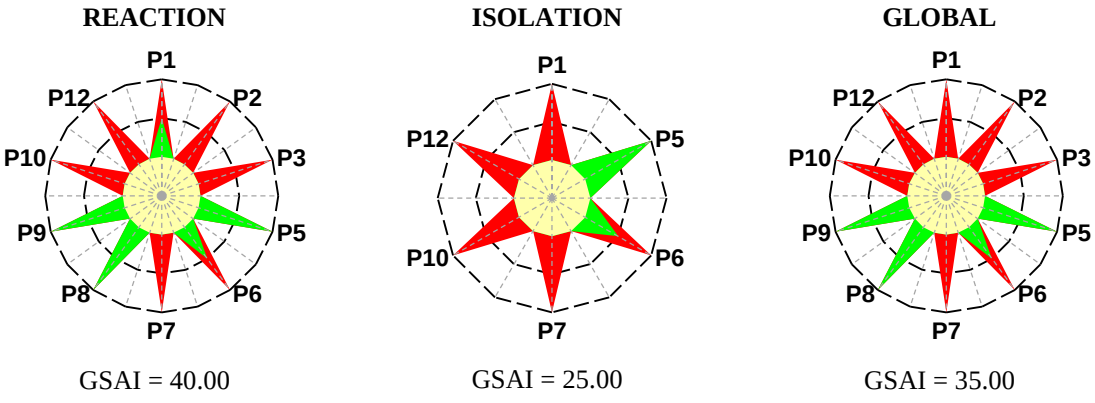

Figure 1. Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate

Construction of the GS

$$V_2O_5 + 2H_2SO_4 + C_2H_6O + 4(Hacac) + 2Na_2CO_3 \rightarrow 2[VO(acac)_2] + 2Na_2SO_4 + C_2H_4O + 5H_2O + 2CO_2$$

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 C[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
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
Vanadium pentoxide (CAS 1314-62-1)	✓			H302, H332, H335, H341, H361, H372, H411	3	3	1
Auxiliary substances							
Solvents							
Water[a,b]	✓	✓		-	1	1	1
Product							
Vanadyl acetylacetonate (3153-26-2)	✓	✓		H302, H315, H319, H335	2	1	1
Waste							
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
Vanadyl sulphate hydrate	✓			H302	2	1	2
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 C[α]

Green Chemistry Principle	Reaction		Isolation		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	2	Vanadyl sulphate hydrate, H302	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	Vanadium pentoxide, H341, H361, H372, H411, sulphuric acid, H314, ethanal, H351		NA	1	Vanadium pentoxide, H341, H361, H372, H411, sulphuric acid, H314, ethanal, H351
P5 Safer solvents and auxiliary substances	3	Water	3	Water	3	Water
P6 Increase energy efficiency	2	0 ºC ≤ T ≤ 100 ºC	2	0 ºC ≤ T ≤ 100 ºC	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	Vanadium pentoxide, H341, H361, H372, sulphuric acid, H314, ethanal, H224, ethanol, H225	1	Ethanal, H224	1	Vanadium pentoxide, H341, H361, H372, sulphuric acid, H314, ethanal, H224, ethanol, H225

[α]s – Score; NA – Not applicable

References

Glidewell, C.; "Metal Acetylacetonate Complexes: Preparation and Characterization" in Woollins, J., Ed.; *Inorganic Experiments*, 2nd ed., Wiley-VCH, Weinheim, 2003; Exp. 3.16.