Synthesis of vanadyl acetylacetonate – Protocol A

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

Reaction. Place 6 mL of distilled water in a 50 mL round-bottomed flask and slowly add 4.5 mL (84 mmol) of concentrated sulphuric acid (about 207% excess) and 15 mL (257 mmol) of ethanol (about 1768% excess). Then add 2.5 g (14 mmol) of vanadium pentoxide, a magnetic stir bar and attach a reflux condenser. Reflux the mixture in an oil bath until a deep blue solution is formed. The heating should last approximately 1-1.5 hours. Cool the solution with running water and filter it. Transfer the filtrate to an Erlenmeyer flask and add, slowly and with stirring, 6.5 mL (63 mmol) of acetylacetone (about 14% excess). Neutralize the mixture with a solution of 10 g (94 mmol) of sodium carbonate (about 243% excess) in 60 mL of water. Add the sodium carbonate solution dropwise with stirring. Place the mixture in an ice bath (about 15 minutes).

Isolation. Filter the precipitate formed and wash it with two 15 mL portions of ice-cold water, ethanol and then with ethyl ether to remove all traces of water from the solid.

Purification. Dissolve about 0.5 g of the compound in 6 mL of dichloromethane, filter and add 20 mL of 40-60 petroleum ether to the solution. Stir and cool in an ice bath for 15 minutes to conclude the precipitation of the compound. Filter, wash with two 20 mL portions of cold petroleum ether and dry.

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.

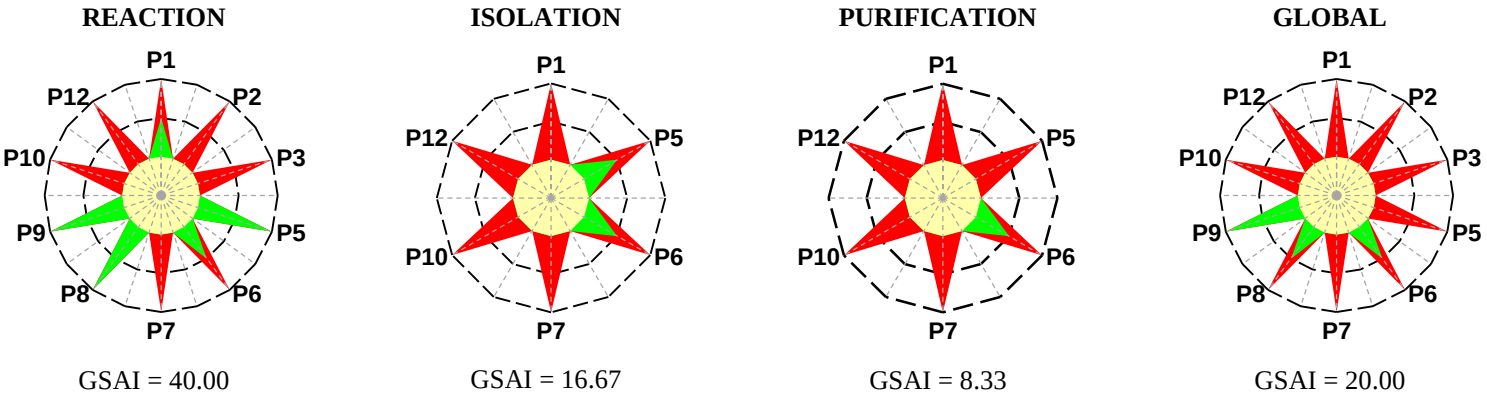

Figure 1. Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate

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 A[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							
Dichloromethane (CAS 75-09-2)			✓	H351	3	1	1
Ethanol[b] (CAS 64-17-5)		✓		H225	1	1	3
Ethyl ether (CAS 60-29-7)		✓		H224, H302, H336, EUH019, EUH066	2	1	3
Petroleum ether (CAS 8032-32-4)			✓	H224, H304, H315, H336, H411	3	3	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
Carbon dioxide	✓			H280	1	1	2
Dichloromethane			✓	H351	3	1	1
Ethanal		✓		H224, H302, H317, H319, H335, H351	3	1	3
Ethanol[b]		✓		H225	1	1	3
Ethyl ether		✓		H224, H302, H336, EUH019, EUH066	2	1	3
Petroleum ether			✓	H224, H304, H315, H336, H411	3	3	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 A[α]

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	2	Vanadyl sulphate hydrate, H302	1	Ethanal, H351	1	Dichloromethane, H351 and petroleum ether, H304, H411	1	Ethanal, H351, dichloromethane, H351 and petroleum ether, H304, H411
P2 Atom Economy	1	Excess of reagents > 10%, formation of by-products		NA		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		NA	1	Vanadium pentoxide, H341, H361, H372, H411, sulphuric acid, H314, ethanal, H351, dichloromethane, H351 and petroleum ether, H304, H411
P5 Safer solvents and auxiliary substances	3	Water	2	Ethyl ether, H302, H336, EUH066	1	Dichloromethane, H351 and petroleum ether, H304, H411	1	Dichloromethane, H351 and petroleum ether, H304, H411
P6 Increase energy efficiency	2	0 ºC ≤ T ≤ 100 ºC	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	1	Substances not renewable
P8 Reduce derivatives	3	One stage		NA		NA	2	Two stages
P9 Catalysts	3	Without catalysts		NA		NA	3	Without catalysts
P10 Design for degradation	1	Substances not degradable	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	Ethanol, H225 and ethanal and ethyl ether, H224	1	Dichloromethane, H351 and petroleum ether, H224	1	Vanadium pentoxide, H341, H361, H372, sulphuric acid, H314, ethanal, H224, ethanol, H225, ethyl ether, H224, dichloromethane, H351 and petroleum ether, H224

[α]s – Score; NA – Not applicable

References

Instituto Superior Técnico – Universidade Técnica de Lisboa, *https://fenix.ist.utl.pt/disciplinas/lq-i/2010-2011/1-semestre* (accessed February 2011).