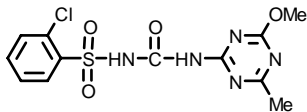


Chlorsulfuron

Uses Chlorsulfuron is a systemic sulfonylurea herbicide for the selective pre- and post-emergence control of broad-leaved and grass weeds in cereal crops.

Common name	Chlorsulfuron
Chemical name (IUPAC)	1-(2-Chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea
CASRN	64902-72-3
Molecular formula	C ₁₂ H ₁₂ ClN ₅ O ₄ S
Molecular weight	357.8
Chemical structure	
Water solubility	587 mg l ⁻¹ (pH 5), 31.8 g l ⁻¹ (pH 7, 25 °C)
K_{oc}	33 (13-54)
Vapour pressure	3 × 10 ⁻⁹ Pa (25 °C)
Log K_{ow}	2.13 (pH 5), 0.10 (pH 7), 0.04 at pH 9 (25 °C)
pK_a	3.6

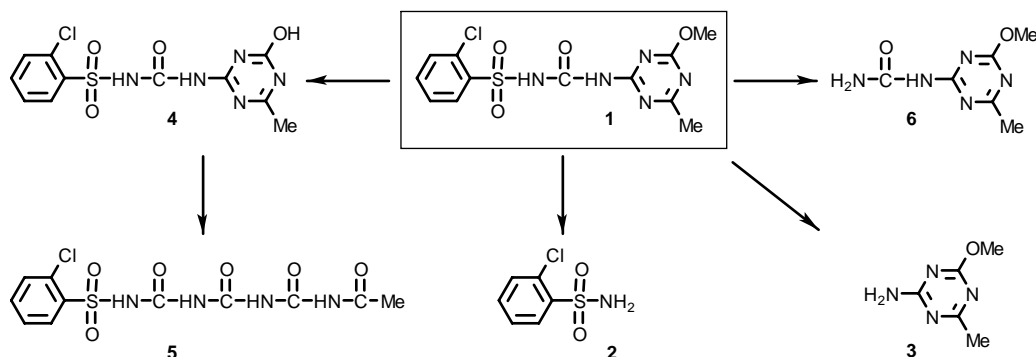
Metabolic pathways

Chlorsulfuron degrades in acidic solution and soil *via* cleavage of the sulfonylurea linkage, *O*-demethylation, and hydroxylation. Mineralisation of chlorsulfuron and its degradation products is mediated by soil microorganisms to yield CO₂ and unextractable soil bound residues. In plants, the primary metabolic pathway involves hydroxylation at either the 5-phenyl- or the methyl carbon of the triazine moiety, followed by carbohydrate conjugation. Due to its rapid elimination, metabolism of chlorsulfuron in animals is minimal. *O*-Demethylation and the cleavage of sulfonylurea linkage were observed. The hydrolytic, photolytic degradation and the overall metabolic pathway of chlorsulfuron in soil, plants, and animals are presented in Schemes 1 and 2.

Chemical degradation

Chlorsulfuron (1) was stable to hydrolytic degradation in neutral and alkaline solutions (pH 7 and 9) at 25 °C with less than 5% degradation after 31 days. However, it was hydrolysed in acidic solution (pH 5) at 25 °C with a DT₅₀ of 24 days (Beyer *et al.*, 1987). The primary hydrolysis reaction was the cleavage of the sulfonylurea linkage, to yield 2-chlorobenzenesulfonamide (2) and 4-methoxy-6-methyl-2-amino-1,3,5-triazine (3) as major products. Other minor hydrolysis reactions included the *O*-demethylation of the methoxytriazine moiety to form 4 [1-(2-chlorophenylsulfonyl)-3-(4-hydroxy-6-methyl-1,3,5-triazin-2-yl)urea] which underwent further hydrolytic cleavage of the triazine ring to yield a unique ring-opened product 5 (Reiser *et al.*, 1991).

No apparent degradation of chlorsulfuron was observed in neutral and alkaline solutions after exposure to natural sunlight. Photolytic degradation of chlorsulfuron in pH 5 buffer was minimal (Dietrich and McAleer, 1989). Products 2, 3, and 6 [(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea], resulting from cleavage of sulfonylurea bond, were detected as minor

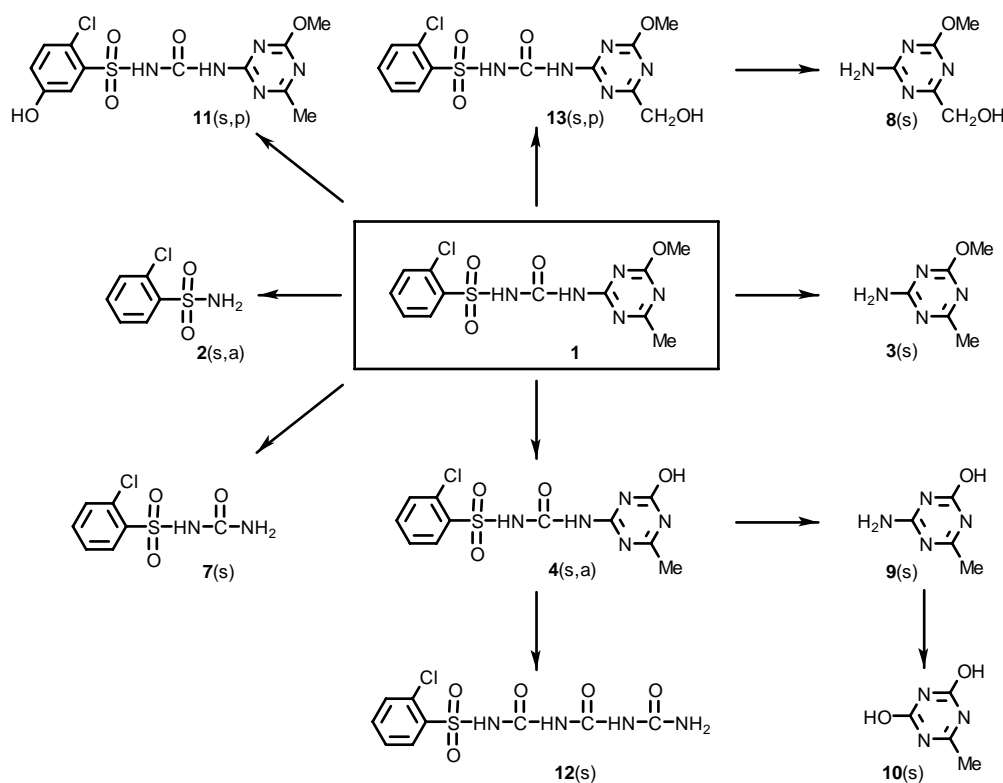


Scheme 1 Hydrolytic and photolytic degradation pathways of chlorsulfuron.

degradation products in solutions exposed to light. The formation of urea (6) appeared to be uniquely related to the presence of light (Strek, 1998).

Degradation in soils

Chlorsulfuron degraded rapidly in a silt loam soil (pH 6.4) at 25 °C under aerobic laboratory conditions, with estimated DT_{50} and DT_{90} values of 20 and 50 days, respectively (Rapisarda *et al.*, 1982). Soil pH has a significant impact on the rate of chlorsulfuron degradation. The DT_{50} of chlorsulfuron in a silty clay loam was 20 days at pH 5.6 and 70 days at pH 7.5 (Fredricksen and Shea, 1986). The degradation rate of chlorsulfuron in a flooded pond sediment/water system (pH 6.7–7.4) under anaerobic conditions was significantly reduced ($DT_{50} > 365$ days) when compared to an aerobic metabolism study using a test soil of similar characteristics (DT_{50} 20 days) (Chrzanowski and Priester, 1991).



Scheme 2 Primary metabolic pathways of chlorsulfuron in soil, plants and animals.

Hydrolytic degradation is the primary dissipation mechanism of chlorsulfuron in the soil environment. Cleavage of the sulfonylurea linkage yielded 2 and 3 as the major degradation products and other minor

secondary hydrolysis cleavage products **7** (2-chlorobenzenesulfonylurea), **8** (4-methoxy-6-hydroxymethyl-2-amino-1,3,5-triazine), **9** (4-hydroxy-6-methyl-2-amino-1,3,5-triazine), and **10** (2,4-dihydroxy-6-methyl-1,3,5-triazine). Microbial processes appeared to be most important in the period immediately following application, but then became less important to the dissipation mechanism, especially under field conditions (Joshi *et al.*, 1985). Minor degradation pathways that involved the intact parent molecule included: hydroxylation of the phenyl-moiety [yielding 1-(2-chloro-5-hydroxyphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea, (**11**)]; *O*-demethylation (yielding **4**) followed by ring opening to yield a unique product **12**.

Chlorsulfuron degraded slightly faster in/on soil (silty clay loam soil, pH 8) surfaces when exposed to a xenon arc light source [DT₅₀ 50 days (light exposed) *vs* 130 days (dark control)] (Rhodes, 1989). Cleavage of the sulfonylurea bridge (yielding **2**, **3**) and *O*-demethylation (yielding **4**) were the major degradation pathways in both light-exposed and dark samples. The only qualitative difference was the detection of small amounts of triazinylurea **6** in the light-exposed samples.

Metabolism in plants

Hydroxylation of the intact molecule followed by carbohydrate conjugation was reported as the primary metabolic pathway of chlorsulfuron in plants. Studies with tolerant monocotyledons such as wheat, oat and barley showed the rapid hydroxylation at the 5-position of the phenyl ring (yielding **11**), whereas sensitive broad-leaved plants such as mustard and sugar beet showed minimal degradation of chlorsulfuron (Sweetser *et al.*, 1982). Compound **11** is still active against the acetolactate synthase enzyme, and requires carbohydrate conjugation to be herbicidally inactivated. Hutchison *et al.* (1984) reported that hydroxylation at the 6-methyl carbon of the triazine moiety yielded 1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-hydroxymethyl-1,3,5-triazin-2-yl)urea (**13**) and its carbohydrate conjugates as major metabolites in tolerant broad-leaved plants such as flax and *Solanum nigrum*. In addition to phenyl hydroxylation and glucoside conjugation, enzymatic cleavage of the sulfonylurea linkage (to yield **2** and **3**) occurred at a faster rate in barley (Brown, 1990). Differences in the rate of hydroxylation, conjugation and the cleavage of the sulfonylurea linkage are the primary selectivity mechanism between tolerant and susceptible plant species (Sweetser *et al.*, 1982).

Metabolism in animals

Rapid elimination of [¹⁴C-phenyl]chlorsulfuron was observed in rats following oral dosing [urine (85%) and faeces (12%), with <1% associated with organs, tissues, and the carcass (Hunt, 1981)]. Due to its rapid

elimination, minimal metabolism was observed since *ca.* 85% of the excreted radioactivity was the undegraded chlorsulfuron together with a small amount of the sulfonylurea linkage cleavage product **2**.

A similar metabolic profile was observed in the lactating goat, where the majority of the orally dosed [¹⁴C-*phenyl*]- and [¹⁴C-*triazine*]chlorsulfuron was readily excreted in the urine (*ca.* 70%) and faeces (*ca.* 7%) (Plowchalk, 1994). All of the radioactivity found in the urine and *ca.* 75% in the faeces was chlorsulfuron. *O*-Demethylation yielded **4** as the major metabolic product in the faecal excreta.

Laying hens eliminated *ca.* 90% of the administered [¹⁴C-*phenyl*]- and [¹⁴C-*triazine*]chlorsulfuron in the excreta. Chlorsulfuron accounted for *ca.* 93% of the eliminated radioactivity (Bodden and Rhodes, 1994). Transfer of ¹⁴C-residues to egg and chicken tissues (*ca.* 0.5%) was negligible.

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