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Chemical Stabilization Study for Sulfonylurea Herbicides

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Sulfonylurea系 除草劑의 化學的 安定性

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ABSTRACT

Sulfonylureas are highly active herbicides which can be applied at very low rate(10-50g/ha) to control broadleaf weeds. The nature of this category of compound is, however, very unstable toward hydrolysis. Therefore, the preparation of these compounds as liquid formulation was not possible. Most of the current formulations of sulfonylurea are in dry forms such as water dispersible granule or wettable powder. Even in these dry forms, the active ingredients also encounter significant chemical decomposition. This study involves the preparation of the sulfonylurea salts by reacting the parent compound with base such as sodium hydroxide. The salt becomes stable toward hydrolysis and it turns soluble when diluted with water. This discovery makes the preparation for liquid formulation or soluble granule of sulfonylurea possible. The stoichiometry of base added to the neutral sulfonylurea is controlled quite precisely. The base has to be added enough to quench the acidic impurities in the technical material and to convert the active ingredient into salt. However, the base should not be overused to cause further saponification of the sulfonylurea salts. The chemical nature of these compounds is presented and the chemical reaction is described. New soluble liquid formulation and solid granule formulation of sulfonylurea are suggested.

Key words : Sulfonylurea herbicide, Formulation, Chemical stability

Overview of Chemical Stabilization Study of Sulfonylurea

This study relates to a novel process for the preparation of sulfonylurea salts for use in liquid and granular formulation with improved chemical stability and biological activity. Such formulations are miscible with water to give true solutions and are useful as preemergent or postemergent herbicides.

Part of this novel process employs water-immiscible halogenated hydrocarbons as solvent in which a heterogeneous reaction between sulfonylurea and metal hydroxide takes place. The process provides very pure salts as products with excellent storage stability.

An alternate process employs a water-miscible

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solvent wherein a homogeneous reaction between a sulfonylurea and metal hydroxide takes place. The process also provides very pure salts. Examples of water soluble solvents are 1-methyl-2-pyrrolidinone, diacetone alcohol, dimethylsulfoxide and dimethylformamide.

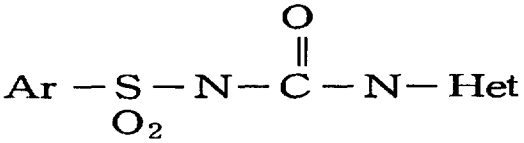
Metal hydroxides used are at controlled amount of alkali or alkaline earth metal hydroxide, methoxide or carbonate. The stoichiometry of base is important in this process. For example, the process can be operated using 1.0 to 1.3 equivalents of sodium hydroxide for every equivalent of sulfonylurea. The reaction can be operated at ambient temperature. The amount of solvent for the reaction is not very critical. Generally 10 to 40 parts by weight of the solvent is used for every part of sulfonylurea in the reaction. The time needed for the completion of this reaction depends on the species of sulfonylurea and the base. When a metal methoxide is used as the base, the reaction requires 4 to 10 hours to reach completion. When a metal hydroxide is used as base, a longer reaction time(10 to 16 hours) is needed.

Depending on the species of sulfonylurea and solvent, the salt formed during the reaction may or may not be dissolved in the solvent. The addition of a drying agent to the reaction mixture is optional and can be carried out anytime during the reaction. The isolated salts of sulfonylurea are very hygroscopic. The salts should be dried under vacuum at ambient temperature and then stored in a desiccator. When the salts are dissolved in water-miscible solvent, the liquid formulations can be easily prepared by adding a controlled amount of surfactant.

The organic solvents for the formulation can be used as obtained commercially if the water content in these solvents is less than 0.5%. Otherwise, it is desirable to dry the solvents by conventional methods. Many of the solvents can be dried over anhydrous magnesium sulfate followed by filtration to remove the drying agent. The liquid formulation can tolerate the presence of small amounts of hydroxylated impurities(e. g. 2% content of 1-propanol) without significant reduction of their stability. A 0.5% content of water in the liquid formulation, for instance, does not reduce the chemical stability of the liquid.

The dry salts and the liquid formulations are very stable. These products do not break down at 50℃ for over 8 weeks. Both of these two products are completely soluble in water. They form clear, true solutions when mixed with water in s spray tank at commercial concentrations of 100 to 10,000ppm. Aqueous solutions of these salts may be stored in a spray tank for at least 2 hours without significant breakdown.

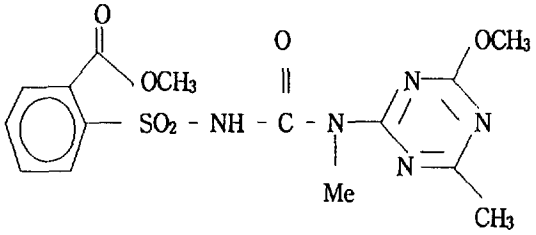
The Figures(1-6) and Tables(1-2) related for this study were in the following.



Ar : Aromatics

Het : Heterocycles

Fig. 1. Chemical structure of sulfonylurea.



- Solid, mp 141℃, purity 94%
- Chemically unstable
- The only proper formulation is WG(Water dispersible granule)

Fig. 2. Chemical characteristics of sulfonylurea herbicide.

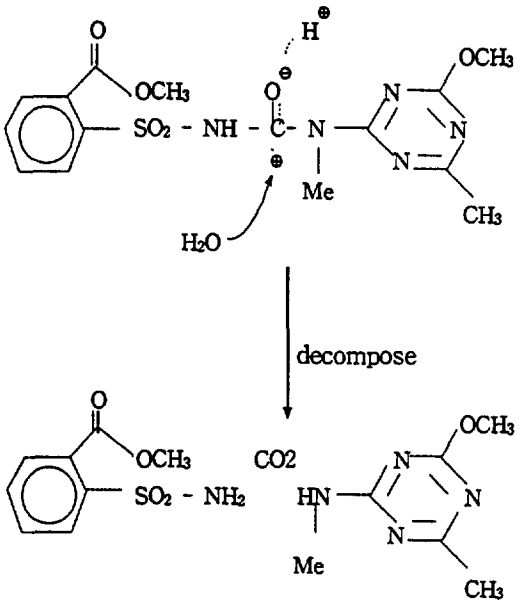


Fig. 3. Hydrolysis reaction of sulfonylurea herbicide.

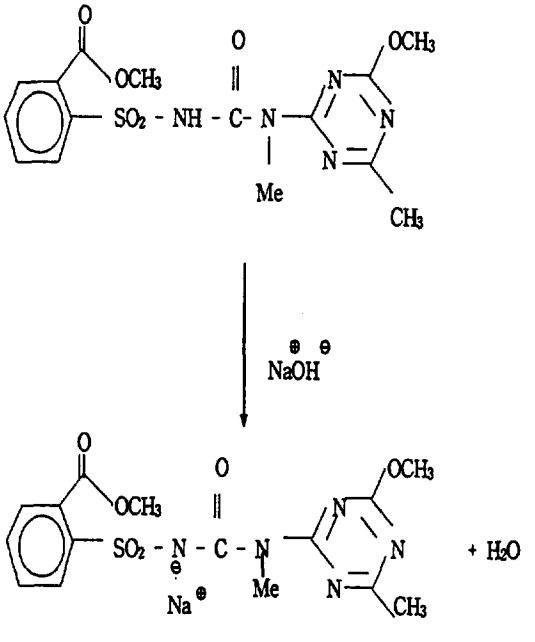


Fig. 4. The formation of salt of sulfonylurea herbicide.

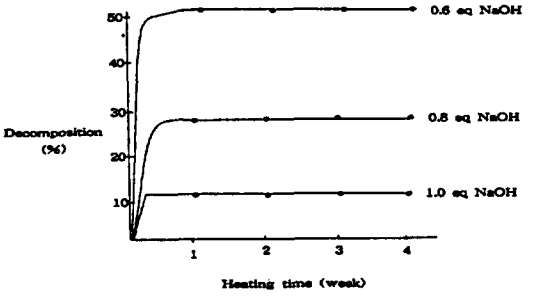


Fig. 5. Degree of decomposition at different amount of sodium hydroxide of sulfonylurea herbicide.

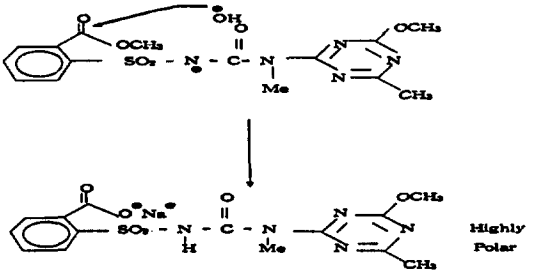


Fig. 6. Further decomposition of Express due to excess sodium hydroxide of sulfonylurea.

Table 1. The relationship between NaOH amount and the decomposition of Express technical of sulfonylurea

NaOH Amount	Decomposition of Express (55℃ / 3 weeks)
0.8 eq	29%
0.9 eq	20%
1.0 eq	11%
1.1 eq	5%
1.15 eq	0%
1.2 eq	2%
1.3 eq	17%

Table 2. New theory of Express of sulfonylurea herbicide

New theory
· Salts of Express are stable Only neutral Express is not stable Stability : K = Na = Li >> H
· The Solvent can contain water up to 1.5% without causing the decomposition of Express

REFERENCES

1. Chia-Chung Chen. 1987. "Process for Preparing Salts of Sulfonylurea Herbicides", US Patent Application # 86867, August 19, 1987; European Patent Application # 304282, February 22, 1989.
2. Chia-Chung Chen and Richard H. Rider. 1988. "Improvement of The Corn Phytotoxicity of Alkyl di-t-butylphosphonotrithioate Insecticides", ICI Americas, Western Research Center.
3. Chia-Chung Chen and Richard H. Rider. 1989. "Study of Chemical Stability of lambda-Cyhalothrin in The Premix Granular Formulation with Fonofos", ICI Americas Western Research Center.