These pore volumes are in agreement with the helium–mercury displacement values for the pellets as shown in Table II.

Helium–mercury displacement methods are not useful for measuring the pore volume of porous powders. The isotherm method, using V_s, may provide a method for measuring pore volumes of powders as well as pellets.

Consideration of the V_s data for the various samples suggests the following interpretation. The original powder (UP) consists of porous granules. V_s is a measure of the intra-granular pore space and does not include significant inter-granular space. In the pelleting operation these granules are packed together and crushed to some extent. Inter-granular space is effectively eliminated in the pellets. Subsequent grinding of the pellets simply forms granules again, without changing the intra-granular pore volume.

This interpretation is supported by the following observations:

(a) The pore volume of pellets measured by helium–mercury displacement agrees with the V_s value.

(b) The V_s value of the original H-G powder is decreased by only 12% on pelleting, whereas the bulk volume of the powder is reduced by more than 75%.

(c) The V_s values for the pellets and the ground pellets are in good agreement.

Estimates of the number of layers held by the adsorbent at saturation (V_s/V_m) give values for H-A and H-G of 12.3 and 5.6 layers, respectively. Chemically these catalysts are nearly identical. Hence it is not likely that the solid surface forces of H-A extend twice as far as the forces of H-G.[13] A more tenable explanation is that V_s simply represents the available volume of pores below a critical pore size and V_s/V_m is a measure of the average pore radius.

Furthermore, the number of layers held by H-G apparently changes from 6.6 to 5.6 on pelleting, and it is improbable that the chemical nature of the solid surface is altered during this process.

Summary

Nitrogen adsorption–desorption isotherm studies have been made at low temperatures with supported catalysts in the powder and pellet forms.

1. Hysteresis effects are very similar for both forms of two catalysts widely different in area. The pore structure responsible for the hysteresis effect is not produced by pelleting nor is it affected by subsequent grinding to 100-mesh powder.

2. Hysteresis extends from 0.4 relative pressure to p_0. V_s may be determined more precisely on desorption than on adsorption. Pore volumes calculated from V_s data are in agreement with those obtained in helium–mercury displacement measurements. Determinations of pore volume by the isotherm V_s method indicate that intra-granular pore volume only is measured. The isotherm method described may thus provide a technique for measuring pore volumes of particles in the finely divided state.

3. For the systems studied the number of layers deposited at p_0 is apparently limited not by solid surface forces but by the pore volume available.

(13) Harkins and Jura, THIS JOURNAL, **66**, 919 (1944), have found that ten layers of nitrogen are adsorbed on a non-porous TiO_2 (anatase) sample. They attribute this film thickness to solid surface forces.

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[CONTRIBUTION FROM PURDUE UNIVERSITY]

Heterocyclic Derivatives of Sulfamide[1]

BY ALBERT FUHRMAN[2] WITH ED. F. DEGERING

The chemistry of substituted sulfamides and their methods of preparation have been reviewed by Audrieth and collaborators.[3] Recently, Wheeler and Degering[4] described a series of substituted sulfamides, prepared by the action of dimethyl and diethylsulfamyl chlorides upon aromatic amines.

The present project deals with the preparation of heterocyclic derivatives of sulfamide and is a continuation of the work of Wheeler and Degering.

Little has been reported on the physiological action of sulfamide derivatives. Aeschliman[5] reported that tetraethylsulfamide in small doses has a slight analeptic action. In view of the antimalarial activity exhibited by certain sulfamides and the current interest in this field, the compounds prepared have been submitted for testing for antimalarial and general pharmacological activity.

The compounds described in this paper were prepared, for the most part, by the action of dialkylsulfamyl chloride on a heterocyclic amine dissolved in either benzene or pyridine. 4,4′-Sulfonyldimorpholine was prepared from sulfuryl chloride and morpholine. N-(Dimethylsulfamyl)-phthalimide was prepared from dimethylsulfamyl chloride and potassium phthalimide.

(1) Abstracted from a thesis presented to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, June, 1944.

(2) Du Pont Fellow, 1944–1945.

(3) Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49–94 (1940).

(4) Wheeler with Degering, THIS JOURNAL, **66**, 1242 (1944).

(5) Aeschliman, Festschrift Emil C. Barrel, 1936, pp. 246–254.

TABLE I

HETEROCYCLIC DERIVATIVES OF SULFAMIDE

	Compound	M. p., °C.[a]	B. p.[b] °C.	Mm.	Yield, %	Formula	Nitrogen, % Calcd.	Found	
1	N,N-Dimethyl-4-morpholinesulfonamide	49–50			76	$C_6H_{14}N_2O_3S$	14.4	14.3	14.3
2	N,N-Diethyl-4-morpholinesulfonamide		110	0.5	97	$C_8H_{18}N_2O_3S$	12.6	12.6	12.5
3	4,4'-Sulfonyldimorpholine	141–142.5			76	$C_8H_{16}N_2O_4S$	11.9	11.7	11.8
4	3,4-Dihydro-N,N-dimethyl-1(2)-quinolinesulfonamide		140	0.3	86	$C_{11}H_{16}N_2O_2S$	11.7	11.6	11.6
5	N,N-Dimethyl-N'-2-pyrimidylsulfamide	217–219			47	$C_6H_{10}N_4O_2S$	27.7	27.2	27.1
6	N,N-Diethyl-N'-2-pyrimidylsulfamide	217–220			29	$C_8H_{14}N_4O_2S$	24.3	24.0	24.4
7	N'-Antipyryl-N,N-dimethylsulfamide	198–199			93	$C_{13}H_{18}N_4O_3S$	50.5[c]	51.0	
							5.81[d]	5.81	
8	N'-Antipyryl-N,N-diethylsulfamide	184–185			93	$C_{15}H_{22}N_4O_3S$	16.6	16.5	16.4
9	N-(Dimethylsulfamyl)-phthalimide	174.5–175.5			78	$C_{10}H_{10}N_2O_4S$	11.0	11.0	11.1
10	N,N,2-Trimethyl-1-piperidinesulfonamide		94	0.5	98	$C_8H_{18}N_2O_2S$	13.6	13.4	13.5
11	N,N,4-Trimethyl-1-piperidinesulfonamide	54–55			97	$C_8H_{18}N_2O_2S$	13.6	13.5	13.4
12	N,N-Diethyl-4-methyl-1-piperidinesulfonamide		109	0.3	92	$C_{10}H_{22}N_2O_2S$	12.0	11.7	11.7

[a,b] Melting and boiling points are uncorrected. [c] % Carbon. [d] % Hydrogen; nitrogen determinations proved unsatisfactory.

The sulfamide derivatives of substituted piperidines are low melting solids or liquids. They are soluble in the common organic solvents and are best recrystallized from petroleum ether. The liquids are stable and may be purified by distillation under reduced pressure.

The properties of the other heterocyclic derivatives depend upon the ring system in question. In general, they melt fairly high and are only slightly soluble in organic solvents.

Experimental

The methods employed in preparing these derivatives may be illustrated by two examples.

N,N-Diethyl-N'-2-pyrimidylsulfamide.—A mixture of 35 g. (0.33 mole) of 2-aminopyrimidine and 57.2 g. (0.33 mole) of diethylsulfamyl chloride in 150 ml. of dry pyridine was allowed to stand overnight at room temperature. The solid dissolved to give a red solution. This was then heated for three hours on a steam-bath and allowed to stand at room temperature for two hours. A solution of 13.2 g. (0.33 mole) of sodium hydroxide in 60 ml. of water was added and the mixture was evaporated under reduced pressure until the pyridine was removed, water being added to maintain the volume. The solution was then acidified to complete the precipitation of a light colored solid (22 g. or 29%). Attempts at recrystallization were unsuccessful. It was purified by dissolving it in dilute sodium hydroxide solution, treating with Norite, filtering, and precipitating with dilute hydrochloric acid. After repeating this procedure for two more times, the product was white and melted at 217–220° (uncor.) with shrinking at 198°.

N,N,2-Trimethyl-1-piperidinesulfonamide.—A solution of 60 g. (0.606 mole) of 2-methylpiperidine in 150 ml. of benzene was cooled in an ice-bath. Stirring was started and 43.5 g. (0.303 mole) of dimethylsulfamyl chloride was added dropwise during a period of fifteen minutes. The mixture was then allowed to stand overnight at room temperature. The red solution was filtered and the residue was washed with warm benzene. The combined filtrate and washings were washed with dilute hydrochloric acid, dried, and evaporated under reduced pressure yielding a red oil weighing 61.4 g. or 98% of the theoretical. Attempts to crystallize the oil failed. It was distilled at 94° (0.55 mm.) (uncor.) to a colorless oil.

The compounds synthesized, together with some of their properties, are listed in Table I.

Unsuccessful attempts were made to prepare sulfanilides from 2-amino-4-methylthiazole and 2-amino-4-thiazolone.

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Summary

Twelve new heterocyclic derivatives of sulfamide have been prepared and characterized.

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