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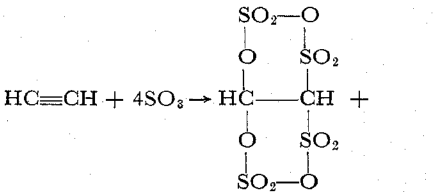
Sulfonation with Sulfur Trioxide

Derivatives of Acetaldehyde Disulfonate

The reactive aldehyde group, plus ease of halogenation, makes this compound a versatile and practical tool for preparing unusual sulfonates, both monomeric and polymeric

Acetylene reacts readily with sulfur trioxide to form an addition compound, which upon aqueous hydrolysis yields acetaldehyde disulfonic acid (ADS) (*6*, *7*, *12*, *13*) (flow diagram, page 927):



$$3H_2O \rightarrow OCHCH(SO_2OH)_2 + 2H_2SO_4$$

Because acetaldehyde disulfonic acid is both easily prepared and contains a highly reactive aldehyde group, it may be of commercial value for sulfoalkylating a variety of organic compounds to yield sulfonates with uses such as ion exchange resins or surface-active agents. However, little serious attempt had been made to establish its utility (*3*). Accordingly, its reactions and derivatives were studied in these laboratories.

ADS is conveniently used in two forms. The monohydrated potassium salt (KADS) is easily isolated (*7*) as a white, nonhygroscopic, stable, free-flowing crystalline solid, insoluble in organic solvents but soluble in water, forming a 1% solution at 25° C., and a 20% solution at 100° C. For condensation reactions conducted in aqueous acid medium, ADS may also be used in the form of crude acetylene–sulfur trioxide (or oleum) reaction mixture which has been carefully hydrolyzed to appropriate acid strength (*5*). This procedure obviates the necessity for forming and isolating the potassium salt, but implies the availability of acetylene and sulfur trioxide or oleum at the point of use.

Literature Background

Subject	Ref.
Unsuccessful attempts to reduce KADS	(*12*)
KADS brominated (but not chlorinated)	(*1*)
Chloromethionate made in very low yield	(*2*)
Cleavage of sulfonate group from methionates	(*13*)
ADS forms tanning agents with phenols	(*8*)
Resorcinol gives ion exchange resins with ADS	(*14*)

Chlorination

The chlorination of ADS is not mentioned in the literature, but it has been converted to the bromo derivative (*1*). In a typical preparation of the chloro compound, 149 grams of KADS was slurried in 150 ml. of water with mechanical agitation at 40° C. in a three-necked laboratory reaction flask. A stream of chlorine was introduced to an uptake of 36.5 grams, during which the temperature rose spontaneously to 60° C. Evaporation to dryness of the reaction mixture gave a 97.5% yield of chloro KADS monohydrate, as determined by analysis for potassium, sulfur, and chlorine.

$$OCHCH(SO_3K)_2 + 2Cl \rightarrow OCHCCl(SO_3K)_2 + HCl$$

Chloro KADS is a stable, white, crystalline solid, insoluble in organic solvents. In water it forms a 20% solution at 25° C. and a 50% solution at 100° C.; it is therefore much more soluble than

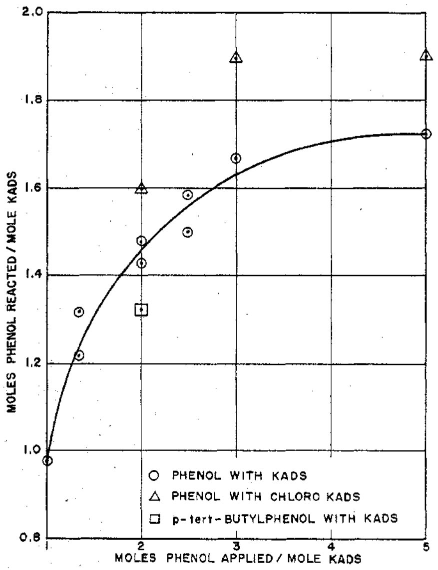


Figure 1. Chemical factors determine maximum attainable degree of reaction of phenols with KADS

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the unchlorinated compound. Presence of the aldehyde group was proved by the formation of a potassium bisulfite adduct of correct analysis. As in ADS, chloro ADS can be prepared without going through the potassium salt by chlorinating at room temperature the carefully hydrolyzed acetylene–sulfur trioxide reaction product—for example, one containing 15% ADS and 40% sulfuric acid (*9*). Behavior of the chloro KADS differs from that of the unchlorinated compound in several respects.

Alkaline reagents convert KADS rapidly and quantitatively to potassium methionate, many derivatives of which have been prepared via its disulfonyl chloride (*4*). Chloro KADS undergoes this reaction even more easily than KADS, because aqueous ammonia effects cleavage of the former, but not of the latter.

$$\mathrm{OCHCH(SO_3K)_2 + KOH \rightarrow HCOOK + CH_2(SO_3K)_2}$$

$$\mathrm{OCHCCl(SO_3K)_2 + NH_4OH \rightarrow HCOONH_4 + ClCH(SO_3K)_2}$$

The chloromethionate was previously prepared in very low yield by another procedure (*2*). A number of chloromethionate derivatives have been reported (*2, 13*).

Reduction

Unsuccessful attempts to reduce the aldehyde group in salts of ADS are reported (*12*). However, in this study, reduction could be effected easily using formaldehyde in a crossed Cannizzaro reaction (*10*) to yield the novel ethanoldisulfonate:

$$\mathrm{OCHCH(SO_3K)_2 + CH_2O + KOH \rightarrow HCOOK + HOCH_2CH(SO_3K)_2}$$

This reaction proceeds quantitatively in spite of the extreme ease with which alkali promotes the cleavage of KADS to methionate in the absence of formaldehyde. Chloro KADS, on the other hand, does undergo preferential cleavage. In a typical preparation, 596 grams of KADS, 300 grams of 37% aqueous formaldehyde, and 200 ml. of water were warmed to 55° C. with good agitation in a reaction flask. A solution of 146 grams of potassium carbonate in 150 ml. of water was added dropwise with agitation over 1.25 hours. After addition, the temperature was gradually raised to 95° C. over 1 hour and held there with agitation for 2 hours; during this time the solid did not completely dissolve, but did change in crystalline form. The reaction mixture was poured in 500 ml. of 95% ethanol and the solid product was filtered after cooling. The filter cake was then washed with a liter of 95% ethyl alcohol to remove potassium formate. The product, after drying, weighed 538 grams (96% of theory). Analysis for potassium and sulfur checked the theoretical.

Table I. The Amylbenzene–ADS Reaction Product Is an Effective Wetting Agent

Alkyl Group on Benzene	Surface Tension[a]		Draves Sinking Time, Sec.	
	0.3	0.1	0.3	0.1
Ethyl	38.2	...	..	...
Isopropyl	37.9	...	..	...
tert-**Butyl**	41.7	...	..	...
sec-**Butyl**	33.1	38.5	..	...
sec-**Amyl**	31.2	33.6	4	14
tert-**Octyl**	31.1	31.7	..	33
Dodecyl[b]	44.0	...	..	>45
Nacconol				
NR	34.4	35.6	23	...
NRSF	36.1	...	14	33

[a] As dynes/cm. at 25° C. in distilled water at weight per cent as given. [b] Detergent alkylate.

Potassium ethanoldisulfonate is a white, free-flowing, crystalline solid, insoluble in organic solvents, but soluble in water to yield a 30% solution at 25° C. Although the hydroxyl group is, as expected, very unreactive, it can be esterified with acetic anhydride using a trace of sulfuric acid catalyst, or with caproyl or palmitoyl chlorides in the presence of pyridine. The last two esters yield aqueous solutions which foam.

Condensation with Alkylbenzenes

Alkylated benzenes were found to condense with KADS in the presence of sulfuric acid (*5*) with the loss of one sulfonate group:

$$\mathrm{2\,RC_6H_5 + OCHCH(SO_3K)_2 \xrightarrow{H_2SO_4} (RC_6H_4)_2\,CHCH_2SO_3K + H_2O + KHSO_4}$$

Cleavage of a sulfonate group, also observed during reaction with phenols, is not unexpected in the light of similar behavior noted by others for several derivatives of methionic acid (*13*). The experimental procedure is as follows:

KADS (0.1 mole) was dissolved in 96% sulfuric acid (90 grams) in a reaction flask equipped with agitation and cooling. At 5° C. the alkylbenzene (0.22 mole, 10% excess) was added dropwise over about 20 minutes, followed by digestion at not over 7° C. for 3 to 4 hours. The cooling bath was removed and stirring was continued for 2 hours, during which time the temperature rose to about 40° C. and then declined to room temperature. The reaction mixture was added to water (200 ml.), which led to separation of an oily layer of the product monosulfonate in free acid form. This layer was separated, neutralized with any desired base, and evaporated to dryness to yield the final products which in most cases were light yellow friable solids readily soluble in water. Yields varied from 60 to 90% of theory. Analytical and titration data on the products were found to be consistent with the above equation.

Several of the sulfonates so prepared are listed in Table I. The *sec*-amyl derivative shows good wetting power, being more effective than the commercial materials used for comparison.

The reaction product of acetylene and sulfur trioxide (1 mole acetylene: 4 moles free sulfur trioxide in 65% oleum) can be used for this reaction instead of KADS, as shown with the mixture of alkylbenzenes (alkyl mainly C_6 and C_9) cheaply available as a by-product in the manufacture of dodecylbenzene detergent alkylate. The hydrocarbon, comprising 72% aromatics with the remainder inert paraffins, was mixed with water (25% by weight) and then treated with the acetylene-oleum reaction product with good agitation and cooling in the range 5° to 15° C. After addition, the temperature was allowed to rise slowly to 40° C. with continued agitation. Paraffins were next removed by steaming. The sulfonate is separated from the spent acid layer in the reactor by decantation, and then neutralized. The sodium salt of this sulfonate showed detergent properties, since an experimental "built" formulation gave soil removal closely comparable to that obtained in comparison runs made with commercial products.

Chloro KADS reacted with alkylbenzenes in a similar manner.

Condensation with Phenols

Reaction of ADS with phenolic compounds to yield water-soluble tanning agents has been reported (*8*). Reaction with resorcinol, followed by treatment with formaldehyde, forms an ion exchange resin (*14*). None of these products mentioned in the literature was characterized.

During the present study, KADS was reacted with a series of mono- and polyhydric phenols, including various alkylated and chlorinated derivatives. The reaction was usually conducted by refluxing several hours at 100° to 110° C. in 20% hydrochloric acid; less reactive phenols—for example, 2,4-dichlorophenol or salicylic acid—were reacted at 50° C. in 95% sulfuric acid. Unreacted phenol was recovered by steam distillation or by solvent extraction, and the aqueous hydrochloric acid was removed by evaporation. Sulfuric acid was removed either by layer separation, or by precipitation as calcium sulfate.

The final products are easily friable, nonhygroscopic solids.

Only two of the phenols studied (2,4-dichlorophenol and 2,4,5-trichlorophenol) reacted at a definite 2:1 molar ratio in a manner analogous to the alkylated benzenes:

$$2C_6H_3Cl_2OH + OCHCH(SO_3K)_2 \xrightarrow{H_2SO_4} (C_6H_2Cl_2OH)_2CHCH_2SO_3K + H_2O + KHSO_4$$

This is attributed to the fact that, of all the phenols studied, these two had only a single reactive position remaining on the ring.

The other phenols all reacted at a maximum ratio lower than 2:1, indicating the formation of polymeric products. Cleavage of one sulfonate group always occurred during condensation.

With five phenols (phenol, catechol, resorcinol, hydroquinone, and phloroglucinol) the polymers could be obtained in either water-soluble or water-insoluble form, depending upon the ratio of reactants used. Insoluble products formed at 0.67 mole of the phenol (or less) per mole of KADS (*9*); the use of a larger proportion of phenol gave a water-soluble product. It was therefore concluded that only phenols with at least three reactive ring positions can yield insoluble resins, and then only by the application of sufficient aldehyde to react with all three positions. The insoluble polymers showed activity as ion exchange resins (*9*).

The reaction of phenol itself with KADS was studied in some detail, with main conclusions as follows:

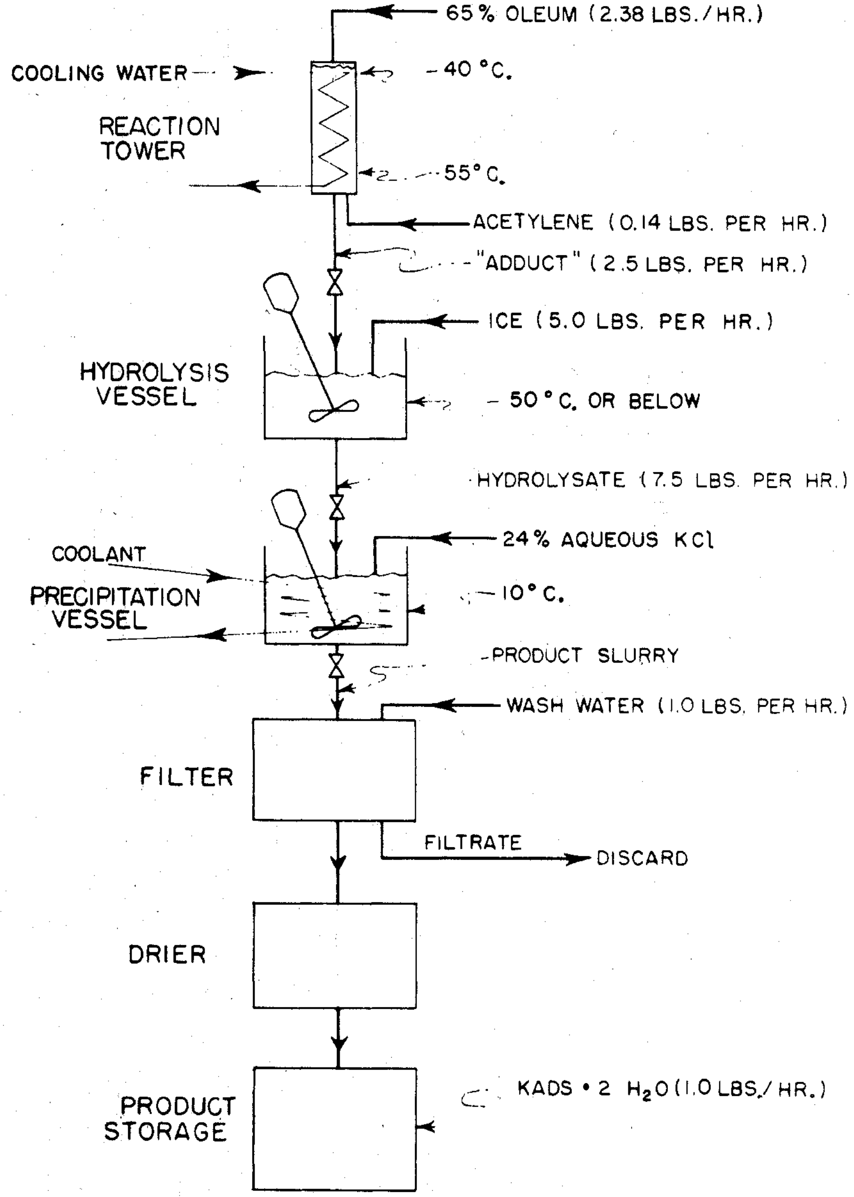
1. The number of moles of phenol reacting per mole of KADS is determined primarily by the excess of phenol employed, and approaches 1.75 as the top limit. Even at a 1:1 ratio, a small quantity (0.03 mole) of phenol remains unreacted. The data are shown in Figure 1.
2. Reaction time has no effect on the ratio reacting over the range tested (3 to 7 hours).
3. The quantity of 20% hydrochloric acid used per mole of KADS has no appreciable effect on the ratio reacting over the range studied (250 to 1200 grams).
4. An acid medium is essential for reaction, which does not occur in neutral or alkaline medium.
5. The oleum-acetylene reaction product, carefully hydrolyzed with water to yield 15% ADS and 36% sulfuric acid, can be substituted for KADS.
6. In forming the water-insoluble resin, equimolar formaldehyde could be substituted for KADS at a total 0.67 (or less) phenol-to-aldehyde ratio. Table II shows that an expected lowering of sulfur content of the resin occurs.

Table II. Phenol and KADS Form Insoluble Resins, with or without Formaldehyde

Mole KADS	Mole Formaldehyde	Sulfur, %
0.39	0.61	12.6
0.44	0.56	13.0
0.47	0.53	12.9
0.55	0.45	13.1
0.68	0.32	14.3
1.00	0	15.1

It is apparent that chemical factors determine the maximum possible reacting ratio. In Figure 1, phenol reacts with chloro KADS at a substantially higher ratio than with KADS. *p-tert*-Butylphenol, on the other hand, reacts at a lower ratio with KADS than does phenol.

The water-soluble phenolic polymers undergo the usual reactions of phenols, including nitration, sulfonation, halogenation, and coupling with diazonium compounds. The hydroxyl groups were reacted with benzoyl chloride and benzenesulfonyl chloride. The chlorinated phenolic derivatives of ADS and chloro ADS, made either by reaction with chlorinated phenols, or by chlorination of the condensation products, have shown activity as fungicides, mothproofing agents, and bactericides for slime control in paper mills (*11*).



A small scale pilot plant was used for producing dipotassium acetaldehyde disulfate on a continuous basis

Several alkyl substituted phenolic derivatives have surface activity, (Table III); however, they are less effective than those compounds derived from the alkylated benzenes.

Table III. A Long Chain, or Disubstitution, Greatly Reduces Wetting Power of Alkylphenol–ADS Reaction Products

Phenol Used	0.3[a]		0.2		0.1		0.05	
	D[b]	T[c]	D	T	D	T	D	T
m-Ethyl	13	34	20	35	300	39	...	42
p-tert-Butyl	20	34	24	35	52	43	335	47
p-tert-Amyl	13	37	18	39	39	42	236	46
p-tert-Octyl	>600	34	...	34	...	35	...	36
Thymol	>600	41	...	43	...	49	...	54

[a] Concentration in weight per cent. [b] Draves sinking time in seconds. [c] Surface tension as dynes/cm. at 20° C.

Mercaptal Formation

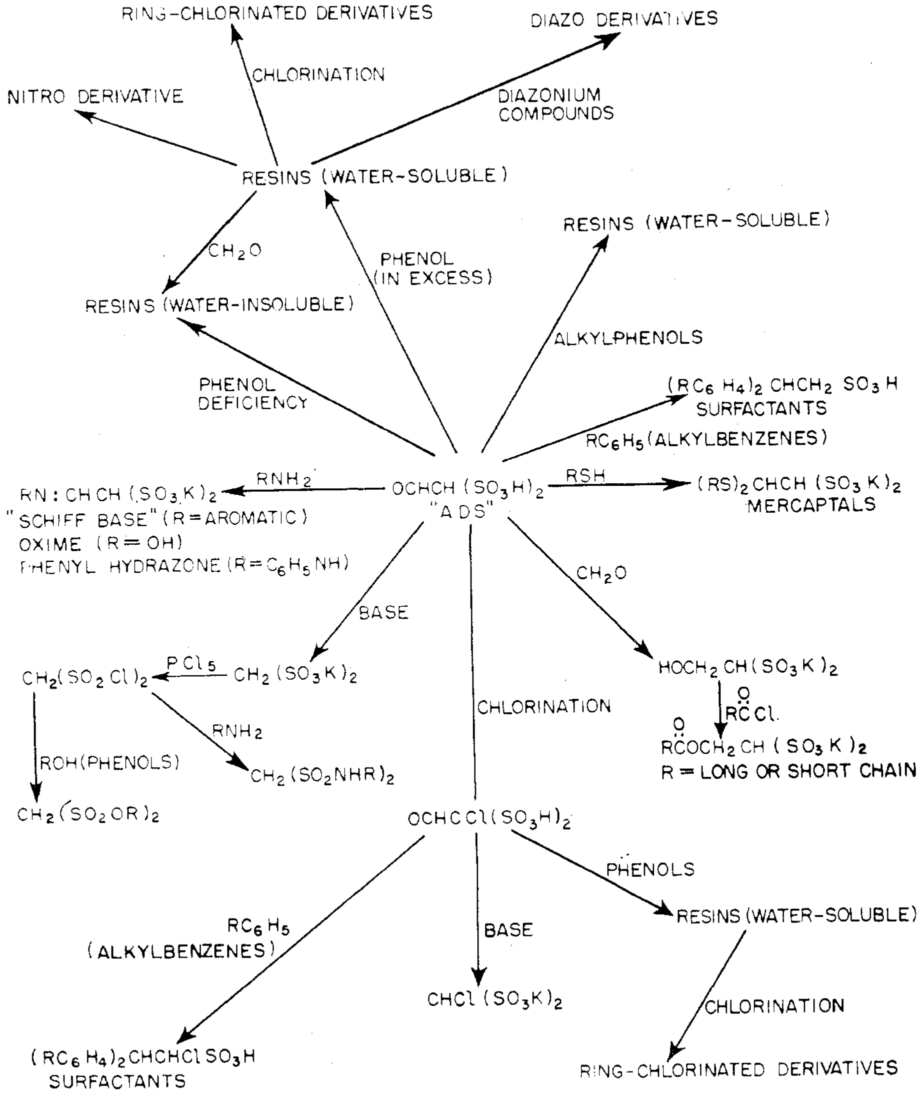
Mercaptals are formed in good yield from thiophenol or benzyl mercaptan by agitating finely powdered KADS with the thiol at 80° C. for 6 hours in concentrated hydrochloric acid suspension:

$$2RSH + OCHCH(SO_3K)_2 \xrightarrow{H+} (RS)_2CHCH(SO_3K)_2 + H_2O$$

Analysis for potassium and sulfur checked the theoretical for both products. *o*-Mercaptobenzoic acid reacted similarly in the presence of 75% sulfuric acid, but not with hydrochloric acid. Mercaptals could not be obtained from *tert*-butyl- and *tert*-dodecylmercaptan. Chloro KADS did not react with benzyl mercaptan. The mercaptals are only slightly soluble in water.

Preparation of KADS

Material used in this study was in part prepared by the procedure shown in the flow diagram of small scale pilot plant. The method is simple and convenient to operate, being well suited to continuous production. In actual practice on a small scale, continuous operation was employed through the hydrolysis stage, batch processing being employed thereafter. Similar yields were noted irrespective of whether the first two steps were run batchwise or continuously. The method was also adaptable for larger scale operation.



Principal reactions and derivatives of acetaldehyde disulfonic acid

Conclusion

Acetaldehyde disulfonate, easily prepared from acetylene and sulfur trioxide is a raw material of unusual versatility. These reactions and derivatives, shown schematically, include data from the literature as well as from this study.

Literature Cited

(1) Backer, H. J., *Rec. trav. chim.* **48,** 571–6 (1929).
(2) *Ibid.*, **49,** 729–34 (1930).
(3) General Chemical Division, Allied Chemical Corp., Morristown, N. J., Product Data Sheet **KA-1.**
(4) *Ibid.*, **MDA-1.**
(5) Gilbert, E. E., Otto, J. A. (to Allied Chemical and Dye Corp.), U. S. Patent **2,506,417** (May 2, 1950).
(6) *Ibid.*, **2,515,444** (July 18, 1950).
(7) *Ibid.*, **2,552,421** (May 8, 1951).
(8) Ott, K. (to Chemische Fabriken vorm. Weiler-ter-Meer), Ger. Patents **383,189** (Oct. 11, 1923); **397,405** (June 24, 1924).
(9) Otto, J. A. (to Allied Chemical and Dye Corp.), U. S. Patent **2,590,449** (March 25, 1952).
(10) Otto, J. A., Gilbert, E. E. (to Allied Chemical and Dye Corp.), *Ibid.*, **2,571,286** (Oct. 16, 1951).
(11) *Ibid.*, **2,597,171** (May 20, 1952).
(12) Schroeter, G., *Ann.* **303,** 114–32 (1898).
(13) *Ibid.*, **418,** 161–257 (1919).
(14) Wassenegger, U. S. Patent **2,319,359** (May 18, 1943).

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