[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VISKING CORPORATION]

THE PREPARATION OF ALIPHATIC NITROSULFONATES. I

MARVIN H. GOLD,[1] LEONARD J. DRUKER,[2] RONALD YOTTER, C. J. B. THOR, AND GERHARD LANG[3]

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Heath and Piggott have disclosed the reaction of nitroölefins with sodium bisulfite to produce aliphatic nitrosulfonates (1) and in general agree with the results obtained in these laboratories. However several observations were noted and new procedures developed in these laboratories which were not disclosed in the earlier paper. The present report will describe these observations and procedures and will tabulate the data for a number of new salts of nitrosulfonic acids prepared in these laboratories.

The nitroölefins were easily prepared by a vapor phase pyrolysis of the appropriate acetate ester (2) and bisulfite was added to the nitroölefins in order to produce the desired β-nitrosulfonates. However, the first few experiments in this direction were unsuccessful until it was discovered that the minimum *p*H 5.4 was necessary in order for the addition to take place (3). A detailed study of this reaction then revealed that upon addition of a nitroölefin to bisulfite solutions of lower than *p*H 5.4, the *p*H of the reaction mixture would decrease. Furthermore only half the nitroölefin would be absorbed by an equimolar quantity of bisulfite solution. Very little was done to identify this reaction product aside from determining that it was a highly water-soluble, hygroscopic material. When nitroölefin was added to bisulfite solutions above *p*H 5.4, the *p*H of the reaction mixture would rise. Inasmuch as the *p*H of pure bisulfite solutions ranges between 3.8 and 4.9,[4] the solution at *p*H 5.4 is then a mixture of bisulfite and sulfite. Thus in the case of the normal reaction, the bisulfite is used up, leaving behind a solution of sulfite which normally has a higher alkalinity.

This limiting *p*H effect in the addition of bisulfite to nitroölefins is apparently an unusual phenomenon and as indicated by Heath and Piggott (1) may be attributable to an oxygen effect. These authors believe that air-oxidation converts sulfite to sulfate ion. However, Mayo and Walling (4) have pointed out in the case of unsaturated hydrocarbons that the *p*H effect is actually an evidence of a peroxide effect and occurs only upon the addition of bisulfite to unsaturated hydrocarbons. At the present time this question has not been satisfactorily resolved.

It was soon found that if the reaction mixture was allowed to rise much above *p*H 7.5, the nitrosulfonate did not crystallize as completely from the reaction mixture as it did at lower *p*H's. Further examination of the mother liquors showed that the nitrosulfonate acted as a buffering agent by neutralization

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[1] Present Address: Aerojet Engineering Corp., Azusa, California.

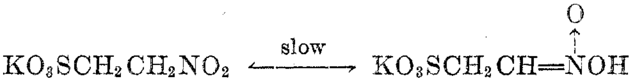
[2] Present Address: Minnesota Mining and Manufacturing Corp., St. Paul, Minnesota.

[3] Present Address: Monsanto Chemical Co., St. Louis, Mo.

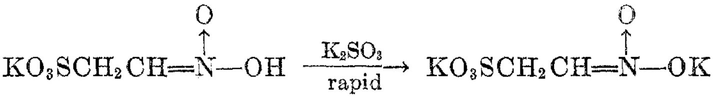
[4] These data were obtained by measuring the *p*H of the solutions of a number of C. P. samples of sodium bisulfite and potassium metabisulfite.

of the enol form. The excess base apparently reacts with enolic nitrosulfonate to produce a stable aci-salt which can be isolated to give a compound of definite melting point and analysis. This reaction is illustrated by equations 1, 2, and 3, using nitroethylene as the simplest nitroölefin.

1. $CH_2{=}CHNO_2 + KHSO_3 \longrightarrow KO_3SCH_2CH_2NO_2$

2. 

$$KO_3SCH_2CH_2NO_2 \xleftrightarrow{\text{slow}} KO_3SCH_2CH{=}\overset{\overset{O}{\uparrow}}{N}OH$$

3. 

$$KO_3SCH_2CH{=}\overset{\overset{O}{\uparrow}}{N}{-}OH \xrightarrow[\text{rapid}]{K_2SO_3} KO_3SCH_2CH{=}\overset{\overset{O}{\uparrow}}{N}{-}OK$$

Reacidification of the enol salt with a weak acid regenerates the free aci-form which then reverts back to the normal nitrosulfonate. Thus, in order to isolate the nitrosulfonates in the best yields, it was found necessary to return the reaction mixture to *p*H 6 or 7 by bubbling in a stream of sulfur dioxide.

Sometime afterwards it was found that the synthesis could be greatly simplified by eliminating the step requiring the preparation of nitroölefins. By this method alkaline sulfite solutions (of *p*H 8 or higher) would react directly with acetate esters of β-nitro alcohols in a double decomposition reaction.

4. $NO_2CH_2CH_2OAc + Na_2SO_3 \rightarrow NO_2CH_2CH_2SO_3Na + NaOAc$

This reaction takes place very readily and gives good yields. It has the disadvantage of requiring fractional crystallization in order to separate the nitrosulfonate completely from the acetate salt.

The next simplification resulted when it was found that a bisulfite solution which was at least *p*H 5.4 would react directly with a β-nitro alcohol to produce the nitrosulfonate (5):

5. $NO_2CH_2CH_2OH + NH_4HSO_3 \rightarrow NO_2CH_2CH_2SO_3NH_4 + H_2O$

The success of this last reaction suggested the idea that perhaps even the nitro alcohol could be eliminated as an intermediate in the reaction. It was soon found that a reaction could be made to occur between a primary nitroparaffin and an aldehyde in the presence of a sulfite at greater than *p*H 6.0 (6). This reaction gave excellent results and was used in preparing large quantities of the nitrosulfonates. It must be noted in this reaction that where formaldehyde is the aldehyde for the reaction, the sulfite used cannot be an ammonium salt. This is important in order to avoid the soluble complex between formaldehyde and ammonium ion which probably is composed of one or a mixture of any of the following: hexamethylene tetramine, the aldimine, or aminomethane sulfonic acid.

The reaction of a nitroparaffin, sulfite, and formaldehyde may be termed a "sulfonomethylation" reaction, similar in many respects to the "chloromethylation" reaction. With the higher aldehydes the reaction would be a "sulfonalkylation". Such a reaction is not peculiar to the nitroparaffins. Other examples of the sulfonoalkylation reaction with active methylene groups (4) or aromatic nuclei (7) are well illustrated in the literature.

EXPERIMENTAL

A. ADDITION OF BISULFITE TO NITROÖLEFINS

Determination of critical pH values. A number of potassium bisulfite solutions were prepared by dissolving 60 g. of potassium hydroxide in 200 ml. of distilled water. Sulfur dioxide was then bubbled into the solution until the requisite *p*H was attained. To these solutions was then added 100 g. of 2-nitro-1-butene while keeping the reaction temperature below 40°. The unreacted nitrobutene was separated from the aqueous layer and the aqueous portion was worked up by concentration under reduced pressure or by cooling in ice to effect crystallization. With all solutions initially below *p*H 5.35, no potassium 2-nitrobutane-1-sulfonate could be isolated. The product at low *p*H was a highly water-soluble, hygroscopic material which has not been identified.

In reaction 5, Table I, only 18 g. (8.1%) of potassium 2-nitrobutane-1-sulfonate was obtained, whereas in reactions 6 and 7, this was the major product, isolated in high yield.

TABLE I

ADDITION OF $KHSO_3$ TO 2-NITRO-1-BUTENE

EXPT. NO.	INITIAL *p*H	FINAL *p*H	RECOVERED NITROBUTENE, G.
1	2.5	1.5	50
2	4.5	3.6	50
3	4.9	2.0	50
4	5.2	2.0	50
5	5.35	2.5	35
6	5.40	6.5	0
7	5.5	6.4	0

Preparation of various nitrosulfonates. In general the nitrosulfonates were easily prepared by adding the nitroölefin to an excess of ammonium or alkali bisulfite initially at *p*H 6.2 to 6.8. The temperature of the reaction mixture was maintained in the range of 10 to 60° depending upon the nature of the nitroölefin. (Nitroethylene requires a lower temperature such as 10–15°, whereas ω-nitrostyrene adds more readily at 40–50°). The ammonium and potassium salts are among the least soluble and frequently crystallize from solution upon cooling. The sodium salts and many of the 1-nitro derivatives require concentration under reduced pressure in order to supersaturate the solutions. The resulting crystalline salts may be purified by recrystallization from water or alcohol-water mixtures. The yields range from 60 to 98%.

A number of cations other than alkali or ammonium have been introduced by one of the following methods:

1. The ammonium salt was evaporated with an equivalent amount of the desired hydroxide, soluble oxide, or carbonate.
2. The free acid was obtained in solution by ion exchange over Zeo-Karb resin (Permutit Co.) and this solution was treated with the requisite amine, hydroxide, oxide, or carbonate.

The nitrosulfonates prepared by any of the above methods as well as those mentioned below, are listed in Table II.

Formation of a sodium enolate. A solution of 130 g. (1.03 moles) of sodium sulfite in 600 cc. of water was at *p*H 9.79 (glass electrode). The solution was stirred rapidly and 100 g.

of 2-nitro-1-butene was added dropwise while keeping the reaction temperature at 40°. The resulting solution was then concentrated under reduced pressure to give a mass of crystals, m.p. 190° with decomposition.

Anal. Calc'd for $C_4H_7NNa_2O_5S$: Na, 20.2. Found: Na, 19.6.

When a portion of this crystalline product was redissolved in water and the solution acidified with dilute acid, the normal sodium sulfonate was recovered.

B. REACTION OF AN ALKALI SULFITE WITH A NITRO ESTER

Potassium 2-nitroethane-1-sulfonate. A solution of 112 g. of potassium hydroxide in 150 ml. of water was treated with sulfur dioxide to *p*H 9. Then 121 g. of 2-nitroethyl-1-acetate (8) was added dropwise while stirring and maintaining the reaction temperature at 30°. A crystalline product separated during the addition. The resulting mixture was treated with sulfur dioxide to *p*H 6 and then cooled in an ice-salt bath. The crystalline product weighed 147 g. (76.2%). An ether wash of the crystalline product and an ether extract of the filtrate yielded no unreacted ester upon evaporation.

TABLE II

SALTS OF β-NITROSULFONIC ACIDS

	M.P., °C. WITH DEC.[a]	ANALYSES					
		Cation		Nitrogen		Sulfur	
		Found	Calc'd	Found	Calc'd	Found	Calc'd
$NO_2CH_2CH_2SO_3NH_4$	191.5–192.5			16.20	16.23	19.11	18.63
$NO_2CH_2CH_2SO_3K$	196–198	20.2	20.4			17.2	16.8
$CH_3CH(SO_3NH_4)CH_2NO_2$	141–143			14.57	15.05	17.43	17.22
$CH_3CH(NO_2)CH_2SO_3NH_4$	190–191			14.46	15.05	17.04	17.22
$CH_3CH(NO_2)CH_2SO_3K$	199–200	18.1	18.8			15.5	15.5
$C_6H_5CH(SO_3NH_4)CH_2NO_2$	130–131						
	170–171			11.20	11.29	12.90	12.90
$C_2H_5CH(NO_2)CH_2SO_3NH_4$	203–206			13.51	13.99	16.03	15.91
$C_2H_5CH(NO_2)CH_2SO_3Na$	225	11.0	11.2			15.15	15.6
$C_2H_5CH(NO_2)CH_2SO_3K$	232	17.6	17.7			14.1	14.5
$[C_2H_5CH(NO_2)CH_2SO_3]_2Ba$	260	27.5	27.4			10.3	10.0
$[C_2H_5CH(NO_2)CH_2SO_3]_2Ca$	>300	9.94	9.9	7.22	6.95	15.55	15.85
$[C_2H_5CH(NO_2)CH_2SO_3]_2Co$	210–211	13.33	13.9	6.26	6.62		
$C_2H_5CH(NO_2)CH_2SO_3Tl$	191–192			3.54	3.62	8.52	8.27
$C_2H_5CH(NO_2)CH_2SO_3\cdot$Brucine	187–190			7.64	7.27	5.56	5.58
$C_2H_5CH(NO_2)CH(C_3H_7)SO_3K$	229–230	15.3	14.9	4.9	5.3	12.4	12.2
$C_3H_7CH(SO_3K)CH_2NO_2$	—	16.9	16.6			13.5	13.6

[a] All melting points are uncorrected.

C. REACTION OF BISULFITE WITH NITRO ALCOHOLS

Potassium 2-nitrobutane-1-sulfonate. Potassium hydroxide (106 g., 2 moles) in 200 ml. of water was treated with sulfur dioxide to *p*H 6.5. Then 119 g. of 2-nitro-1-butanol (from Commercial Solvents Corp.) was added dropwise while maintaining a temperature of 45°. After stirring for five hours at 45° the solution was acidified with sulfur dioxide. Then the reaction mixture was cooled in ice and the product was isolated. A yield of 203 g. (92%) of relatively pure product was obtained.

D. THE SULFONALKYLATION REACTION

Potassium 2-nitrobutane-1-sulfonate. Potassium hydroxide (112 g.) in 200 ml. of water was treated with sulfur dioxide to *p*H 6.5. To this solution of potassium sulfite was added 89 g. of 1-nitropropane. Then, while maintaining the reaction temperature at 60°, 81 g. of 37% formaldehyde was added dropwise. The mixture was stirred one hour at 60° and then brought back to *p*H 7 with sulfur dioxide. A crystalline product separated; yield, 166 g. (73.3%) of potassium 2-nitrobutane-1-sulfonate, m.p. 224–226° (compared to 232° for the pure compound).

Potassium 5-nitroheptane-4-sulfonate. Potassium hydroxide (120 g.) in 180 ml. of water was treated with sulfur dioxide to *p*H 8. One mole (89 g.) of 1-nitropropane was then added, followed by 72 g. of redistilled butyraldehyde. After heating the mixture with stirring for two hours at 80–90° a clear solution resulted. Sulfur dioxide was then introduced to $<$ *p*H 7. Some inorganic products separated at first and were removed by filtration. Then upon cooling overnight in a refrigerator the product crystallized. The mixture of stereoisomers was recrystallized three times from water giving a pure isomer, which was apparently the major product; m.p. 229–230° (d).

SUMMARY

Four methods are given for the preparation of aliphatic β-nitrosulfonates. These are:

1. The addition of bisulfite to nitroölefins.
2. The metathesis of sulfite with the ester of a β-nitroalcohol.
3. The reaction of a bisulfite with a β-nitroalcohol.
4. The reaction of a primary nitroparaffin, an aldehyde, and a sulfite.

CHICAGO 38, ILLINOIS

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