the solution and this corresponds to 96.6% of the iodine originally added.

Summary

The reaction of benzyl iodide with three organic disulfides, in the presence of mercuric iodide or ferric chloride, has been studied.

Four sulfonium compounds, in the form of the addition complex with the metallic halide, were prepared. Two of these are new compounds.

A mechanism for the reaction has been proposed.

PRINCETON, N. J. RECEIVED FEBRUARY 8, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ALABAMA]

Reactions of Sulfur and Vapors of Organic Compounds at Different Temperatures[1]

BY GEO. D. PALMER, S. J. LLOYD, W. P. MCLURE, NORMAN LEMAISTRE, W. S. WARING AND L. W. BACHMAN

The preparation of a new series of sulfur dyes by a vapor method using benzene and other organic compounds in contact with molten sulfur at temperatures *above* 300° has been reported.[2] With similar apparatus, we are now able to report the preparation of two new classes of sulfur organic compounds prepared at temperatures *below* 300°.

Experimental

Preparation of New Sulfur Organic Compounds.—We find that the vapors of many organic substances, including benzene, toluene, aniline, phenol, etc., when passed through molten sulfur at 240–260° form resinous sulfur dyes (A) which are in some cases rubber-like after purification, whereas at 260–300° non-resinous sulfur organic compounds (B) which are not dyes result. These are brown to black powdery solids, insoluble in sodium sulfide and carbon bisulfide. Hydrogen sulfide is a by-product, much more being evolved in preparation of A than B. The yields of A are much better than those of B and are comparable to the yields of compounds prepared above 300° (C).[2]

Purification and Analyses.—Eighteen samples were purified with carbon bisulfide, acetone, benzene, and water for 525 hours in large-scale Soxhlet extractors. Analyses for sulfur were made at intervals until the percentage of sulfur in each substance became constant.

Discussion

All sulfur dyes prepared by this vapor method and producing intense colors contain 50 to 83% sulfur. A few aliphatic substances which have yielded small amounts of low-sulfur-content dyes have produced much less intense colors on cotton and rayon.

It appears that the higher the sulfur content of the dye, the less the sodium sulfide (in aqueous solution) required to dissolve it. It also appears that the higher the sulfur content, the more resinous is the material. The resinous property of the chlorobenzene product (A) is lost when it is dissolved in aqueous sodium sulfide, but is regained by precipitation with a mineral acid.

TABLE I

COMPOSITION OF PURIFIED SULFUR ORGANIC SUBSTANCES PREPARED BELOW 300°

Compd. reacting with sulfur	Opt. temp. for prepn., °C.	S, %	N, %	Cl, %
Benzene	260–300	30.95		
Aniline	260–300	30.96	9.63	
Chlorobenzene	240–260	83.44		1.08

TABLE II

PROPERTIES OF DYES PREPARED FROM CHLOROBENZENE AND SULFUR ABOVE AND BELOW 300°

Opt. temp., for prepn., °C.	Phys. form	Color of solid	Soly. in CS_2	Soly. in aq. Na_2S	Color on cot. and rayon
360–444.6	Powd.	Red	Insol.	Sl.	Red-brown
240–260	Res. matl.	Gray-black	Sl.	Fairly	Dark-brown

TABLE III

COMPOSITION OF PURIFIED SULFUR DYES PREPARED AT 360–444.6°

Sample	Compound reacting with sulfur	C, %	H, %	S, %	N, %	O, %
1	Benzene	34.54	0.92	62.46		
2	Toluene	36.17	0.93	62.68		
3	Phenol	34.95	1.97	55.15		7.93
4	Aniline	37.88	1.23	53.38	6.56	

Empirical formulas have been calculated for dyes 1 and 2 in Table III, and a constancy of $C_3H_1S_2$ is indicated. The grouping in these high sulfur content organic substances prepared from hydrocarbons and sulfur at 360–444.6 is apparently similar to the recurrent grouping in the formula of thiokol[3] in that in each case *one* hydro-

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(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) Geo. D. Palmer and S. J. Lloyd, THIS JOURNAL, **52**, 3388 (1930).

(3) J. C. Patrick, *Modern Plastics*, [2] **14**, 46 (1936).

carbon group is attached to *four* sulfur atoms. Thus

$S_2C_2H_4S_2$ (Thiokol)
$S_2C_6H_2S_2$ (Sulfur dye from benzene)

Summary

1. By contacting vapors of organic compounds with molten sulfur *below* 300°, two new classes of sulfur organic compounds have been prepared, with hydrogen sulfide as a by-product.
2. Products prepared at 240–260° are resinous sulfur dyes, while products prepared at 260–300° are non-resinous and are not sulfur dyes.
3. High sulfur content is necessary in the sulfur dyes for the production of intense colors.
4. Additional ideas as to the structure of sulfur dyes prepared by vapor methods have been presented.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 455, AND FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, NO. 217, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Inversion of Sucrose

BY LAWRENCE J. HEIDT AND CLIFFORD B. PURVES

Recently we published data on the rates of hydrolysis of several fructosides including sucrose at 30 to 60° and calculated energies of activation, E, assuming that E did not vary with temperature. At the same time Leininger and Kilpatrick[1] found that in more concentrated solutions of sucrose E was smaller at 30 than at 0°, but that $\mathrm{d}E/\mathrm{d}T$ approached zero as T increased. In addition, their data gave smaller values of E at 5.8 than at 0.5 N hydrochloric acid. Nevertheless, the rate constants obtained by extrapolating their data to our acid concentration of 0.01 N gave, within the limits of error, the same values of E and $\mathrm{d}E/\mathrm{d}T$ between 25 and 35° as our previously published[2] values of $E = 25.75$ kcal. and $\mathrm{d}E/\mathrm{d}T = 0$ between 30 and 60°. They followed the inversion by noting the accompanying contraction of a fixed weight of solution. We used the copper reduction technique to measure the rate of formation of reducing sugars. The divergence of $\mathrm{d}E/\mathrm{d}T$ from 0 obtained by the dilatometric method at temperatures lower than 25° led us to see whether this divergence could also be observed by the copper reduction technique when working in the same range of temperature and at the same concentrations of reactants used in reference 1. We were especially interested in this problem because conclusions like those we drew by comparing activation energies for the hydrolysis of fructosides[2] would be vitiated, of course, if the values of E were determined where $\mathrm{d}E/\mathrm{d}T$ was not zero.

The reagents,[2] experimental procedure[2] and apparatus[3] have been described. Reactions at 10.00° took place in a thermostat kindly lent by Professor Scatchard. Especial care was taken to transfer each sample quickly from the reaction cell to just enough caustic soda solution at 0° so that the resulting solution was neutral to phenolphthalein. These neutral solutions were kept at 0° until analyzed.[2]

Corrections for the sucrose, sodium chloride, and concentrations of the reducing sugars present in the analyses were usually negligible. For example, 5 cc. of a 5% solution of sucrose formed cuprous oxide equivalent to 8 cc. of the 0.002 M sodium thiosulfate[4] and 1 cc. of a 23% solution of sodium chloride increased by 3.5% the cuprous oxide formed by the invert sugar. To reduce titration errors, the estimations of the reducing sugar in each sample withdrawn from the reaction cell were made at several concentrations scattered over the range covered in the calibrations.

Concentrations were referred to a liter of solution at the temperature the sucrose was inverted. Acid concentrations were obtained in each case by titrating with standard base weighed aliquots whose volumes at the temperature of the hydrolysis were carefully measured. Phenolphthalein was used as the indicator. The titrations agreed in every case with calculations based on the dilution of the standardized acid used to make up the sucrose solutions, so no measurable amount of acid was produced or consumed during the inversion.[5]

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(1) Leininger and Kilpatrick, THIS JOURNAL, **60**, 2891 (1938).

(2) Heidt and Purves, *ibid.*, **60**, 1206 (1938).

(3) Heidt, *ibid.*, **61**, 3455 (1939).

(4) In the earlier work[3] this hypo was denoted as 0.002 N.

(5) These titrations, however, would not reveal slight decreases in the pH like those noted in the photosensitized reaction: Heidt, THIS JOURNAL, **61**, 3223 (1939).