mum yield of crystalline dichlorostibine was obtained by further cooling, first in a deep-freeze and finally in a Dry Ice–alcohol-bath. The compound was recrystallized repeatedly from chloroform by dissolving it at room temperature and cooling the solution in a Dry Ice-bath.

The compounds prepared by the above procedure are so indicated in Table I. On reduction, the *p*-methoxybenzenestibonic acid yielded a crystalline product which was probably the dichlorostibine. Attempts at recrystallization invariably resulted in decomposition. No crystalline product was obtained using *m*-bromo-, *m*-chloro-, *m*-carboxy- and *m*-ethoxybenzenestibonic acids.

We have also used the same procedure to reduce stibonic acids previously purified through the pyridinium arylchloroantimonates(V).[8] No advantage over the simpler procedure was found.

Method B.—Schmidt prepared phenyldichlorostibine in small yield by treating an acetic acid solution of stibosobenzene with 5 *N* hydrochloric acid.[1] The following modification has resulted in a substantial increase in yield. Either the crude stibonic acid obtained as an intermediate in method A or a purified stibonic acid[8] was reduced with sulfur dioxide and hydriodic acid as described previously.[2]

The resulting impure stiboso compound was suspended in a minimum amount of chloroform, cooled in a Dry Ice-bath, and treated with a slow stream of dry hydrogen chloride. The amorphous solid was rapidly converted to crystalline dichlorostibine, which was collected on a sintered glass filter cooled with Dry Ice. Recrystallization was achieved as described under method A.

This procedure is technically more difficult than method A, but it probably has a wider range of application. It is of particular value with stibonic acids containing groups which are themselves reduced by stannous chloride, *e. g.*, *p*-nitrobenzenestibonic acid.

m-**Chlorophenyldichlorostibine.**—A number of attempts have been made to obtain this compound. The difficulties encountered were apparently associated with a low melting point and extreme solubility. Both crude and purified *m*-chlorobenzenstibonic acid, as well as a sample recrystallized from benzene, were reduced by method A, but no dichlorostibine was isolated in any case. Similar results were obtained in the reduction of a crude stibonic acid with sulfur dioxide, following the procedure of Blicke and Oakdale.[4c] Method B yielded a crystalline solid which rapidly changed to an oil when removed from the cold filter. All attempts to recrystallize this oil have been unsuccessful. Analysis of the product without recrystallization gave values which approached the theoretical (Calcd. for $C_6H_4Cl_3Sb$: Sb, 40.02. Found: Sb, 39.46). Hydrolysis of this product also yielded analytically pure *m*-chlorostibosobenzene.

m-**Chlorophenyldiiodostibine.**—Crude *m*-chlorostibosobenzene (45 g.) was dissolved in 100 ml. of concentrated hydrochloric acid; the solution was cooled to 0°, and a saturated aqueous solution of potassium iodide was added. The yellow diiodostibine which precipitated was washed with cold water to remove sodium chloride, dried *in vacuo* for three hours, and finally recrystallized several times from chloroform; m. p. 67–68°.

Anal. Calcd. for $C_6H_4ClI_2Sb$: Sb, 25.00; I, 52.10. Found: Sb, 25.02; I, 52.07.

Stiboso Compounds.—A solution of the dichlorostibine in cold absolute alcohol (0.2 mole in 200 ml.) was added dropwise with stirring to a solution of 18 g. of sodium hydroxide in 4 liters of ice and water. The stiboso compound which precipitated was washed with water on a large Buechner funnel until free from chlorides. It was then washed successively with cold alcohol and cold ether and finally dried *in vacuo*. With the exception of *m*-stibosotoluene the yields in each case exceeded 90%. The stiboso compounds prepared are listed in Table II.

Acknowledgments.—*p*-Aminoethylbenzene was obtained through the courtesy of Dr. Arthur Roe and Dr. R. L. McKee, Department of Chemistry, University of North Carolina. The authors also wish to acknowledge the assistance of Miss Marjorie L. Chapman in performing the analyses.

Summary

Improved methods for the synthesis of aryldichlorostibines have been developed. Eight aryldichlorostibines and one diiodostibine have been prepared. The corresponding stiboso compounds were prepared by hydrolysis with aqueous sodium hydroxide.

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[8] Doak and Steinmann, THIS JOURNAL, **68**, 1987 (1946).

[CONTRIBUTION FROM THE SYPHILIS EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, AND SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Disproportionation of Aromatic Stiboso Compounds. III. Effect of Structure[1]

BY H. H. JAFFÉ AND G. O. DOAK

It has long been known that a variation in structure produces a marked effect on the stability of metallo-organic compounds. This received formal recognition by Kharasch and coworkers,[2] who, in studying the effect of structure on the acid cleavage of unsymmetrical organic mercury compounds, established an "electronegativity scale" for a large number of aliphatic and aromatic radicals. The stability of various metallo-organic compounds was predicted on the basis of this scale.[3] Unfortunately this work was based on competitive reactions, a technique which is open to considerable criticism,[4] and which necessarily yields only qualitative comparisons. Further, a scale of this type will have general application only to series of reactions having a constant entropy of activation. Such constancy has never been demonstrated for series containing aliphatic and ortho-substituted aromatic radicals.[5]

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[1] Paper presented in part before the Division of Physical and Inorganic Chemistry at the 113th meeting of the American Chemical Society, Chicago, April, 1948.

[2] Kharasch, *et al.*, *J. Org. Chem.*, **3**, 347, 405, 409 (1939); THIS JOURNAL, **54**, 674 (1932), and earlier papers.

[3] Kharasch and Isbell, *ibid.*, **53**, 2701 (1931); Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

[4] Adkins, in Gilman, "Organic Chemistry," John Wiley & Sons, New York, N. Y., 1943, p. 1074.

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 194.

Since reaction rates of thermal decomposition reactions are a measure of the thermal stability of the compounds involved, the relative values of such rate constants will establish quantitatively a scale of the effect of structure on the stability of the compounds. In the present paper we are reporting such a scale, based on the rates of disproportionation of some aromatic stiboso compounds.

In the first paper of this series[6] we proposed a plausible mechanism for the disproportionation of stibosobenzene. Nevertheless the reaction was catalyzed by impurities introduced in the synthesis, and therefore the absolute rate could not be determined. Since purification of the compound has been found impossible, synthetic methods were developed which avoided introduction of these contaminants.[7] Duplicate preparations of stibosobenzene and several of its substitution products prepared by these methods gave rate constants reproducible within the limits of experimental error; this has been taken for evidence that the catalytic impurities were absent in these preparations. Reproducible rate constants could not be obtained with a few aromatic stiboso compounds, although analytically pure samples were available. In these cases the difficulties were associated with purification of the intermediate aryldichlorostibines, as has been discussed in the previous paper.[7]

Experimental

Materials.—All stiboso compounds used in the present investigation were prepared by hydrolysis of the corresponding aryldichlorostibines with aqueous sodium hydroxide. Details of the method of preparation are described in the preceding paper.[7]

Method.—The reaction rates were determined by the method previously described,[6] but the increased stability of the compounds available necessitated raising the temperature to 100 ± 0.02°. The bis-(diarylantimony) oxide formed was extracted after heating weighed samples of the stiboso compounds for varying time intervals, and the extracts evaporated to dryness *in vacuo*. The amount of product was determined from the weight and antimony analysis of the residue. In this way the course of the reaction was verified. Moreover, several bis-(diarylantimony) oxides were isolated, and their characteristics are reported in Table I.

TABLE I

BIS-(DIARYLANTIMONY) OXIDES, $[(RC_6H_4)_2Sb]_2O$

R	Recrystallization solvent	M. p., °C.	Sb analyses, % Calcd.	Found
p-CH_3[a]	Ether	107[b]	39.02	39.2
p-Cl	Carbon	147	34.51	34.1
H	tetrachloride	82[c]	42.81	42.1

[a] Molecular weight in benzene 565 (calcd. 624.1). [b] Blicke and Oakdale, THIS JOURNAL, **55**, 1198 (1933), give m. p. 101°. [c] Schmidt, *Ann.*, **421**, 174 (1920), gives m. p. 78–80°.

The rate constants were determined by the method of least squares from the equation

$$-\,dx/dt = kx(1 - x)$$

where x is the fraction of the original stiboso compound remaining at time t. All rate constants reported are weighted means[8] obtained from two or more separate preparations of each compound, with the exception of p-nitrostibosobenzene and p-stibosoacetophenone. The thermal stability of these two compounds required the disproportionation to be followed for more than thirty days at 100°. During this period side reactions leading to traces of nitrobenzene and acetophenone, respectively, were observed. The latter was identified as the 2,4-dinitrophenylhydrazone, using a pooled sample from a number of reaction tubes. For these reasons the rate constants reported for these two compounds are subject to a relatively large error.

Results and Discussion

The specific rate constants k for the disproportionation of several aromatic stiboso compounds are reported in Table II, together with their standard errors (s). The relative thermal stability of the compounds, referred to stibosobenzene as unity, is measured by the fraction k^0/k[9] and is given in the last column of Table II. These values establish a quantitative scale of the effect of meta- and para-substituent groups on the stability of these compounds. The rate constants are plotted against Hammett's substitution constants (σ)[10] in Fig. 1. It is seen that the points fall near a straight line, and thus the disproportionation of the aromatic stiboso compounds conforms to Hammett's equation.[10]

$$\log k - \log k^0 = \sigma\rho \qquad (1)$$

Consequently the scale of the thermal stabilities established in this paper is directly related to Hammett's σ-values, and equation (1) can be employed to predict the thermal stability of aromatic stiboso compounds as yet unprepared. This treatment will not be applicable to the aliphatic and ortho-substituted aromatic stiboso compounds since these cannot be expected to possess constant entropies of activation. We believe however that it will be applicable to reactions of other series of metallo-organic compounds. Then a knowledge of the thermal stabilities of a few members of a given series will

TABLE II

THE RATES OF DISPROPORTIONATION OF SEVERAL ARYLSTIBOSO COMPOUNDS (RSbO) AT 100°

R	10^5k	10^5s_k	σ	R. S.[a]
H	13.62	0.41	0	1.00
p-CH_3	19.96	.27	−0.170	0.682
p-Cl	1.104	.023	+ .227	12.34
p-Br	0.9276	.047	.232	14.68
m-Cl	1.314	.122	.373	10.37
p-CH_3CO	0.1673	.016	.536[b]	81.41
p-NO_2	.0864	.017	.778	157.5

[a] Relative Thermal Stability. [b] The σ-value given by Hammett applies only to derivatives of aniline and phenol. The value used here was estimated by reducing the value for amines and phenols in proportion with the reduction found for the p-nitro group.

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[6] Jaffé and Doak, THIS JOURNAL, **71**, 602 (1949).

[7] Doak and Jaffé, *ibid.*, **72**, 3025 (1950).

[8] The rate constant obtained from each preparation was weighted by its invariance.

[9] k^0 is the rate constant for stibosobenzene.

[10] Ref. 5, Chapter VII.

permit prediction of the stability of the remaining members for which σ-values are available.

The value of the reaction constant was determined by the method of Bartlett[11] and was found to be $\rho = -2.9 \pm 0.1$.[12]

Mechanism.—The results obtained in the present study add considerable weight to the mechanism proposed for the disproportionation of the stiboso compounds.[6] Since the substitution constants are a quantitative measure of the electron attracting or repelling properties of radicals, conformance with Hammett's equation implies that the electron distribution in the benzene ring largely determines the relative thermal stability of the compounds studied. In a previous paper[6] mechanisms involving an interface reaction or a reaction in solution were considered. Evidence available at that time did not favor either hypothesis. In each case the rate would be determined by physical properties which would not be expected to be a function of the electron distribution. This fact is a further strong argument against these mechanisms.

The large negative value of the reaction constant ρ further permits the conclusion that the aromatic group is not transferred as a carbanion, since electron attracting substituents would be expected to facilitate the formation of such an anion. The transfer as a carbonium ion cannot definitely be excluded on the basis of the data presented, although the formation of a carbonium ion in the absence of an ionizing solvent is difficult to visualize, particularly under consideration of the greater electronegativity of carbon compared with antimony. It appears more probable that the aryl group is transferred as a free radical. This is in general accord with the known thermal decompositions of other metallo-organic compounds, which generally take place by a free radical mechanism.[13]

The absence of biphenyl in the reaction mixture indicates that the concentration of free radicals must be small at all times. The formation of acetophenone and nitrobenzene from *p*-stibosoacetophenone and *p*-nitrostibosobenzene respectively is consistent with a free radical mechanism, since these compounds may arise from the attack of the radicals on the relatively mobile hydrogen atoms available in the corresponding stiboso compounds.

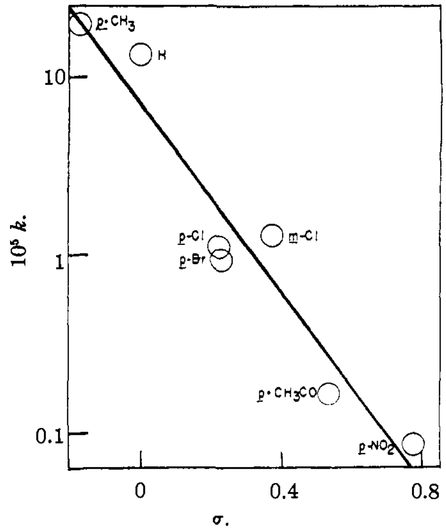

Fig. 1.—Rate constants of the disproportionation of arylstiboso compounds as a function of σ-values.

Acknowledgments.—The authors wish to acknowledge the assistance of Miss Marjorie L. Chapman in performing the antimony analyses, and of Dr. B. G. Greenberg with the statistical evaluations.

Summary

1. The rates of disproportionation of seven aromatic stiboso compounds have been determined at 100° in the solid state.

2. The disproportionation of aromatic stiboso compounds was shown to obey Hammett's equation with a reaction constant of $\rho = -2.9 \pm 0.1$.

3. The data presented permit the prediction of the thermal stability of other aromatic stiboso compounds as yet unprepared.

4. It is predicted that reactions of other series of metallo-organic compounds will also obey Hammett's equation.

5. The mechanism previously proposed for the disproportionation of stibosobenzene is discussed in the light of the data presented, and it is concluded that the phenyl groups are transferred as free radicals.

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[11] Bartlett, *Biometrics*, **5**, 207 (1949).

[12] The error indicated is the 50% confidence interval, (t = 0.727 for 5 degrees of freedom) and this corresponds to the probable error commonly employed.

[13] Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 510.