

increases. This correlation between acidic dissociation and activity is shown to be directly associated with the negative character of the  $\text{SO}_2$  group. In brief, the theory may be stated as follows: the more negative the  $\text{SO}_2$  group of an  $\text{N}^1$ -substituted sulfanilamide derivative, the greater is its bacteriostatic power.

The inductive constants of the various  $\text{N}^1$ -substituents have been evaluated. Based on this method, a quantitative treatment of the theory has been developed. The calculated value of the acid constant for optimum activity agreed very well with the experimental results. The relative activity of the ionic and molecular forms of the sul-

fonamides has also been predicted by this treatment.

Since acid constants are related to both the structure of the  $\text{N}^1$ -substituent and the activity of the derivative, an indirect correlation between structure and chemotherapeutic activity is established. Knowing something about the relative electron attracting power of the  $\text{N}^1$ -substituent, it is possible for the first time to predict the bacteriostatic power of any new sulfanilamide derivative of this type. A discussion of the relation of structure to activity, and a description of the proposed theory and its implications are given.

STAMFORD, CONN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

## Mixed Heteropoly Acid Catalysts for the Vapor Phase Air Oxidation of Naphthalene<sup>1</sup>

BY HENRY TRUEHEART BROWN<sup>2</sup> AND J. C. W. FRAZER

Catalysts prepared from heteropoly acids were first used for the partial oxidation of naphthalene in the vapor phase by Marisic.<sup>3</sup> The chief products from this reaction were phthalic and maleic anhydrides together with traces of naphthoquinone and benzoic acid. The reader is referred to Marisic's paper for a discussion of other catalysts used in this reaction and of the reasons for investigating heteropoly acid catalysts.

The present investigation arose from a consideration of the catalyst prepared from ammonium phospho-vanado-tungstate,<sup>3</sup> which gave considerably higher conversions of naphthalene to phthalic anhydride than either vanadium pentoxide or tungsten oxide alone.

In view of the fact that (1) heteropoly acid ions have a cage-like structure<sup>4</sup> into which only groups of the right size can fit, *i. e.*, octahedrally coordinated molybdenum, tungsten, and vanadium oxide complexes, and that (2) mixed compounds of the phospho-vanado-tungstate type exist, it seemed desirable to attempt the preparation of mixed heteropoly acids which should vary in composition from 12-molybdosilicic acid to 12-tungstosilicic acid wherein the mixed anions should contain both tungsten and molybdenum.

(1) Condensed from a dissertation submitted by H. T. Brown to the faculty of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Standard Oil Company (Indiana), Whiting, Indiana.

(3) Marisic, *THIS JOURNAL*, **62**, 2312 (1940).

(4) Keggins, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934).

It was expected that a series of catalysts prepared from such acids should exhibit coactivation similar to that in ammonium phospho-vanado-tungstate.

### Experimental

**Preparation of the Catalysts.**—The general method employed in preparing the "mixed heteropoly acids" was a stepwise acidification of a solution containing tungstate, molybdate and silicate ions in the desired proportions and then an ether extraction of the product. This method was adapted from North's<sup>5</sup> preparations of 12-molybdosilicic acid with careful attention to all of the precautions which he mentions.

Catalysts were prepared from carefully purified acid crystals of 8–14 mesh size. These crystals were slowly heated in a stream of air to 400° and maintained at that temperature for one hour.

**Preparations of the Heteropoly Acids.**—Because of the importance of this step in the work, detailed directions will be given for preparing a typical "mixed acid" while directions for the others, together with their analyses, are summarized in Table I.

**6-Molybdo-6-tungsto-silicic acid** was prepared by dissolving 12.5 g. sodium molybdate and 17.1 g. sodium tungstate in 100 ml. of water heated to 65°. Then 5 ml. of concentrated hydrochloric acid was added dropwise with mechanical stirring, followed by 2.8 g. of sodium silicate solution (d. 1.375) diluted with a little water. Seventeen ml. of concentrated hydrochloric acid was added dropwise with vigorous stirring and the hot solution was filtered through asbestos to remove a slight precipitate of silica. After cooling, 22 ml. of concentrated hydrochloric acid was added and the clear solution was extracted with ether and the ether layer was purified as directed by North.<sup>5</sup> The

(5) North, in Booth "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, Vol. I, pp. 127–129.

TABLE I

Acid	Preparation				Temp., °C.	Concd. HCl, ml.	Analyses, %					
	Na <sub>2</sub> MoO <sub>4</sub> -2H <sub>2</sub> O in g.	Na <sub>2</sub> WO <sub>4</sub> -2H <sub>2</sub> O in g.	Water- glass d. 1.375 in g.	Vol. of water ml.			MoO <sub>3</sub>		WO <sub>3</sub>		SiO <sub>2</sub>	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	30	..	3.0	120	60	48	..	..	..	..	..	..
H <sub>4</sub> SiMo <sub>9</sub> W <sub>3</sub> O <sub>40</sub>	21	9.6	2.9	100	60	44	63.1	68.5	34.0	28.8	2.9	2.7
H <sub>4</sub> SiMo <sub>6</sub> W <sub>6</sub> O <sub>40</sub>	12.5	17.1	2.8	100	65	39	37.3	36.2	60.1	61.6	2.6	2.2
H <sub>4</sub> SiMo <sub>3</sub> W <sub>9</sub> O <sub>40</sub>	5.6	23.0	2.7	75	70	35	17.0	20.4	80.6	77.0	2.4	2.7
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>		30.0	2.5	60	100	32						

resulting crystals were dried in a vacuum desiccator before use.

**Analysis of the Catalysts.**—A dried sample of each catalyst was ignited below 400° in a porcelain boat and then heated to 270° in a stream of dry hydrogen chloride. This procedure removed molybdic oxide quantitatively<sup>6</sup> as an oxychloride and weighing gave molybdic oxide by difference. Similarly tungstic oxide was removed at about 500° leaving a white residue of silica. The results are given in Table I.

**Apparatus and Experimental Procedure.**—The apparatus employed was that described by Marisc<sup>3</sup> except that only one condenser loosely filled with glass wool was used to catch the condensable products, and the exit gases were analyzed. These gases were dried with phosphorus pentoxide, carbon dioxide was absorbed in soda lime, and "Hopcalite" catalyzed the oxidation of carbon monoxide which was then absorbed in soda lime. The two soda lime towers were weighed to 1 mg. before and after each

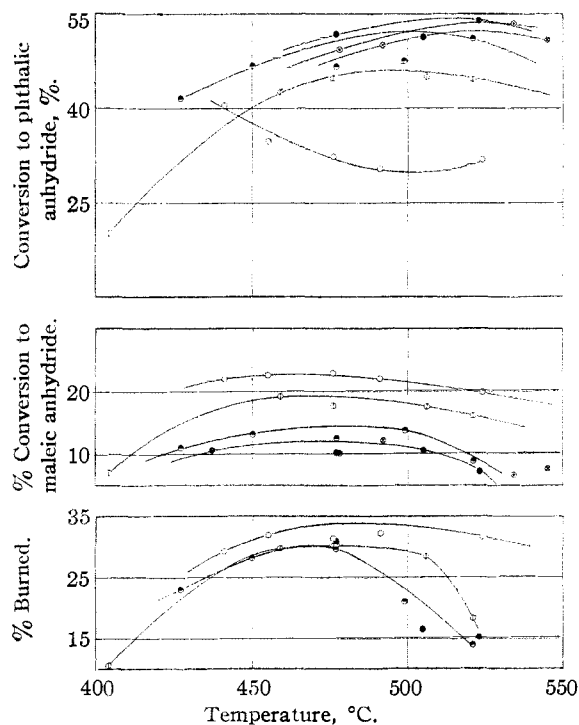


Fig. 1.—Catalyst from H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> at space velocity: ○, 6,850; ⊕, 13,700; ●, 24,000; ⊗, 26,200; ●, 29,200; ⊖, 32,000.

(6) Treadwell and Hall, "Analytical Chemistry," Vol. II, 7th ed., John Wiley and Sons, Inc., New York, N. Y., 1928, pp. 274 and 277.

run. Because of a better air regulator reproducible results were obtained with half-hour runs but otherwise the experimental procedure and analysis of the products were identical with Marisc's.

### Experimental Data

Results for the air oxidation of naphthalene are given in Figs. 1-4.

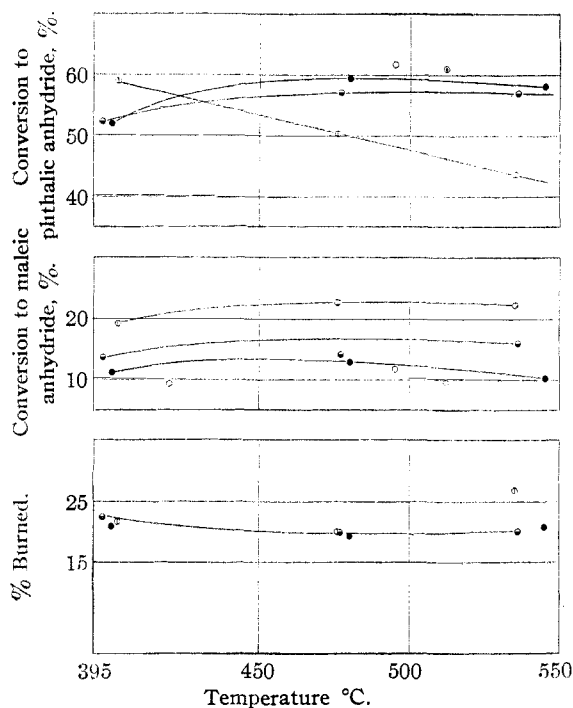


Fig. 2.—Catalyst from H<sub>4</sub>SiMo<sub>9</sub>W<sub>3</sub>O<sub>40</sub> at space velocity: ⊕, 13,700; ●, 24,000; ●, 29,200; ⊖, 42,000; ⊖, 51,000.

**Carbon Monoxide from the Catalytic Oxidation of Naphthalene.**—It was observed in preliminary runs on the 12-molybdosilicic acid catalyst that carbon monoxide makes up a considerable proportion of the exit gases. In a series of runs at 476° the molar ratio of carbon dioxide to carbon monoxide was found to be a function of the space velocity and fell from 2.89 at s. v. 3420 to 1.87 at 8570, remaining constant at 1.87 up to a space velocity of 29,200.

This would seem to indicate that carbon monoxide is produced in large amounts at some stage

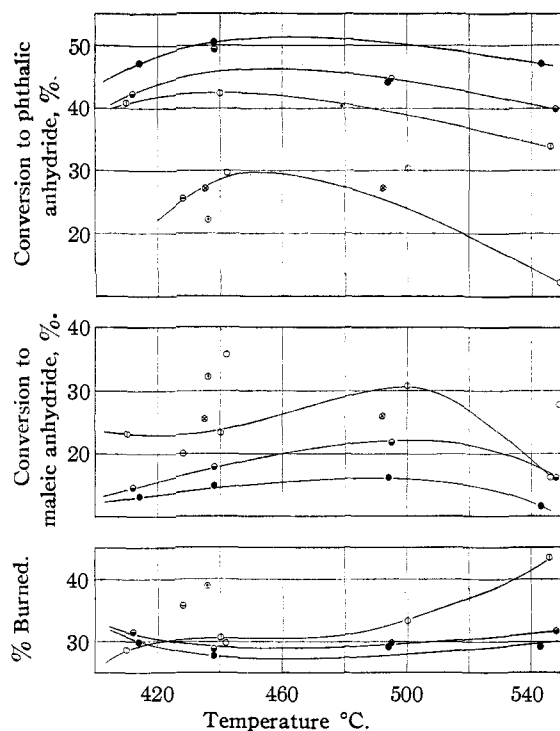


Fig. 3.—Catalyst from  $H_4SiMo_8W_6O_{40}$  at space velocity:  $\circ$ , 8,900;  $\square$ , 13,700;  $\diamond$ , 17,800;  $\otimes$ , 24,000;  $\bullet$ , 31,100;  $\bullet$ , 37,800.

of the oxidation and that part of the carbon dioxide detected comes from the oxidation of carbon monoxide. Later expts. showed that these catalysts are slightly active for the oxidation of carbon monoxide.

**Effect of Carbon Dioxide.**—It was found that the addition of carbon dioxide to the air-naphthalene mixture suppressed the formation of maleic anhydride and increased the amount of phthalic anhydride. Using the catalyst from 12-molybdosilicic acid at  $496^\circ$ , space velocity 24,000 and an air/carbon dioxide ratio of 6/1, 53.8% of the naphthalene was converted to phthalic and 14.1% to maleic anhydride. This represents an increased phthalic yield of 13% over a run under the same conditions with pure air.

**Oxidation of Phthalic Anhydride.**—Weighed samples of phthalic anhydride were vaporized into the air stream and passed over the catalyst from 9-molybdo-3-tungsto-silicic acid under con-

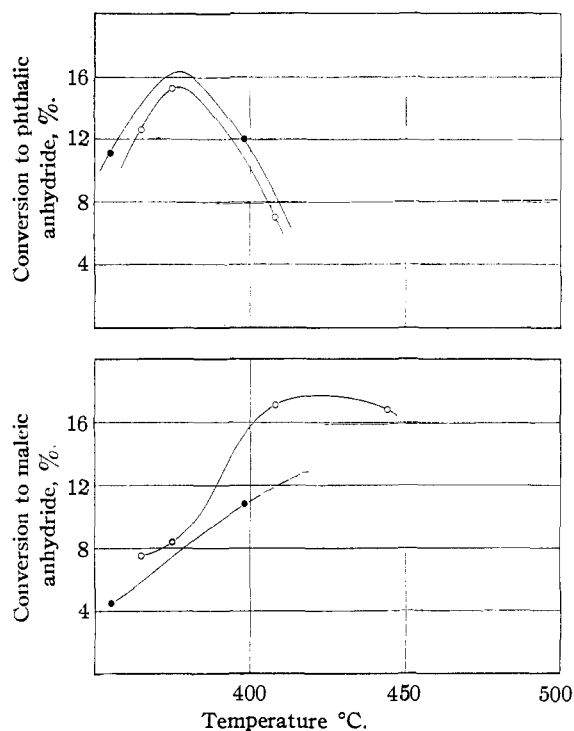


Fig. 4.—Catalyst from  $H_4SiMo_8W_6O_{40}$  at space velocity:  $\circ$ , 24,000;  $\bullet$ , 29,200.

ditions comparable to those in the oxidation of naphthalene. The results of these experiments are presented in Table II (vol. of catalyst was 2 cc.).

**Oxidation of Naphthoquinone-1,4.**—Because it was suspected that naphthoquinone-1,4 might be an intermediate product in the formation of phthalic anhydride, small weighed samples were vaporized and oxidized over the 9-molybdo-3-tungsto-silicic acid catalyst as above. The amount of complete combustion at  $500^\circ$  and s. v. 24,000 was three times as much as naphthalene gave under the same conditions and the yield of phthalic anhydride was much smaller. These experiments seem to indicate that naphthoquinone-1,4 is not an important intermediate between naphthalene and phthalic anhydride.

### Discussion of Results

The experimental results from this work seem to throw little new light on the mechanism of the catalytic oxidation of naphthalene. It seems likely that only a small part of the naphthalene is oxidized to phthalic anhydride via naphthoquinone-1,4. Possibly the other naphthoquinones, 1,2 and 2,6, may be intermediates, but the first decomposes at the melting point and the second was not readily obtainable, so neither could be

TABLE II

Temp., °C.	Space velocity	Phthalic anhydride, g.	Phthalic anhydride		Burned, %
			Not oxidized, %	Converted to maleic, %	
485	24,000	0.2608	56	17.6	26.4
490	36,000	.2525	68	10.0	22.0
492	51,000	.3110	73	8.1	18.9

TABLE III

Catalyst	Temp., °C.	Space velocity	% Conversion to		
			Phthalic	Maleic	Complete combustion
12 Mo	523	29,000	54.0	7.2	15.2
9 Mo-3 W	495	42,000	61.6	11.7	...
6 Mo-6 W	438	37,800	50.5	14.9	27.7
3 Mo-9 W	375	24,000	15.3	8.4	Very high
12 W	410	Any or all	Practically complete combustion		

tested. It may also be concluded that perhaps all of the maleic anhydride results from the oxidation of phthalic anhydride and that with a given catalyst the amount of maleic is a function of the space velocity. If the oxidation data for  $H_4SiMo_9W_3O_{40}$  at  $495^\circ$  are plotted against space velocity it can be seen that decreasing the time of contact increases the yield of phthalic at the expense of the maleic anhydride. At the same time the amount of complete combustion is essentially unchanged. This last fact together with the results from oxidizing phthalic anhydride seems to indicate that phthalic and maleic anhydrides are burned at approximately the same rate and that the reaction is not just a series of steps leading finally to complete oxidation.

The effect of catalyst composition is summarized in Table III, giving conditions for optimum yields.

It may be seen that the effect of increasing the ratio of tungsten to molybdenum in these catalysts is to lower the temperature for optimum yields of phthalic anhydride. The catalyst 9 Mo-3 W gives a maximum yield of 61.6% phthalic anhydride, which is considerably better than the

54% for 12 Mo, at a temperature which is  $28^\circ$  lower. These two effects can hardly be explained by assuming a mixture of crystals of 12 Mo and 12 W and constitute the strongest indication that the catalysts were prepared from mixed acid ions.<sup>7</sup>

### Summary

1. A series of catalysts has been prepared from heteropoly acid crystals containing tungsten and molybdenum.

2. The activities of these catalysts have been studied for the partial oxidation of naphthalene.

3. The catalyst from  $H_4SiMo_9W_3O_{40}$  gave considerably higher conversion to phthalic anhydride than either of the parent acids,  $H_4SiMo_{12}O_{40}$  or  $H_4SiW_{12}O_{40}$ .

4. The addition of carbon dioxide to this air oxidation reaction improved the yield of phthalic and decreased the yield of maleic anhydride.

6. The catalyst from  $H_4SiMo_9W_3O_{40}$  was employed in the oxidation of phthalic anhydride, naphthoquinone-1,4 and carbon monoxide.

(7) An unsuccessful attempt was made to obtain more direct evidence for the existence of mixed acid ions by means of their ultraviolet absorption spectra.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

## The Catalytic Interchange of Groups in Aliphatic Amines. I

BY KENZIE NOZAKI

A number of reactions are known in which the groups attached to a given kind of atom are exchanged between molecules under the influence of certain metal halide catalysts. Two thoroughly studied examples are the migration of alkyl groups in benzene derivatives,<sup>1</sup> and the redistribution of organo-metallic substances, recently investigated by Calingaert and co-workers.<sup>2</sup> The reactions so far observed have been

(1) (a) Jacobsen, *Ber.*, **18**, 338 (1885); (b) Buddelley and Kenner, *J. Chem. Soc.*, 303 (1935); (c) Moyle and Smith, *THIS JOURNAL*, **59**, 1417 (1937).

(2) Calingaert and co-workers, *ibid.*, **61**, 2748 (1939); **63**, 947 (1941).

confined almost exclusively to the exchange of groups attached to either carbon or metals. In this paper we wish to report a case where groups attached to nitrogen are exchanged.

It was found from preliminary experiments that when aliphatic amines are heated in the presence of metal halide catalysts, the alkyl groups and the hydrogen atoms attached to the nitrogen atom may be redistributed. In this redistribution process, all the possible combinations of the alkyl groups and the hydrogen atoms with the nitrogen atom occur. Calingaert and co-workers found similar results with the metal alkyls. Since the