

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° 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° 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.⁷

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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The Catalytic Interchange of Groups in Aliphatic Amines. I

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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,¹ and the redistribution of organo-metallic substances, recently investigated by Calingaert and co-workers.² 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

interconversion of amines is of practical as well as of theoretical importance, it seemed worth while to study the reaction. In this paper some of the work which has so far been carried out is reported.

Experimental Results

Much of the work reported in this paper involves the use of di-*n*-butylamine, which was chosen for study because it is relatively inexpensive, has a moderately high boiling point, and can readily be separated from *n*-butylamine and tri-*n*-butylamine by fractional distillation.

Characteristics of the Reaction.—The reaction described in this paper is apparently free of side reactions below 200°. Above this temperature a slow reaction occurs which produces a high boiling product. However, in all runs reported in this paper, the amount of this reaction was negligible. This side reaction, which is being studied further, is believed to be an alkylation of the alkyl groups of the tertiary amine.

During redistribution, the alkyl groups do not undergo the structural rearrangements which are often observed in Friedel-Crafts reactions.³ Thus, careful observation of boiling points and the preparation of picrate derivatives has indicated that whenever a *n*-butylamine was taken initially, the reaction products were *n*-butylamines and ammonia. The absence of rearrangement within the alkyl groups during the redistribution of organometallics has been reported.⁴

Experiments in Open Vessels.—Experiments were first carried out in which di-*n*-butylamine was heated with a catalyst at atmospheric pressure. Under these conditions the ammonia which was formed in the reaction escaped and was lost. Thus equilibrium was never reached. However, the amount of tri-*n*-butylamine found at the end of any period of heating gave an indication of the amount of redistribution which had occurred.

In Table I are listed the results obtained when di-*n*-butylamine was refluxed with four different substances. It is observed that sulfuric acid has no catalytic effect and that the order of the catalytic activity of the metal halides, $\text{AlCl}_3 > \text{FeCl}_3 > \text{ZnCl}_2$, is the same as has been found for the Friedel-Crafts and allied reactions. Since aluminum chloride was the best catalyst, it was used in all subsequent work. It should be mentioned that di-*n*-butylamine heated alone in a

sealed tube at 300° for several hours showed no evidence of redistribution or decomposition.

TABLE I

THE ACTION OF DIFFERENT CATALYSTS ON DI-*n*-BUTYLAMINE

Catalyst	Moles of catalyst per mole of amine	Reflux time, min.	Composition of reaction products, mole per cent.		
			NH ₂ -(C ₄ H ₉)	NH-(C ₄ H ₉) ₂	N-(C ₄ H ₉) ₃
AlCl ₃	0.126	240	9.7	74.2	16.1
FeCl ₃	.129	240	4.6	89.6	5.8
ZnCl ₂	.124	240	2.1	95.7	2.2
H ₂ SO ₄	.422	1500	0.0	100.0	0.0

In order to obtain some information concerning the nature of the reaction, experiments were carried out in which the dependence of the rate of redistribution on the catalyst concentration was determined. It was found that when the quantity of aluminum chloride added to a given amount of di-*n*-butylamine was doubled, the time necessary for a certain fraction to be converted into tri-*n*-butylamine was decreased to one fourth. For example, the periods of heating required at 164° to produce 0.0072 mole of tri-*n*-butylamine in mixtures in which 0.0075, 0.015 and 0.030 mole of aluminum chloride had been added initially to 0.119 mole of di-*n*-butylamine were one hundred and twenty, thirty and eight minutes, respectively. These results seem to indicate that the reaction is of second order with respect to aluminum chloride concentration.

Experiments were next conducted to determine the effect of time of heating upon the amount of redistribution. In Table II are summarized the results of several runs in which 0.252 mole of aluminum chloride was added per mole of di-*n*-butylamine and the mixture refluxed for the period given. It is observed that, although the rates of formation of *n*-butylamine and tri-*n*-butylamine were probably the same at the start of the reaction, the rate of formation of *n*-butylamine fell off much more rapidly with time than that of tri-*n*-butylamine, and eventually the concentration of *n*-butylamine started to decrease. Substitution of the data into integrated rate expressions indicated that the rate of tri-*n*-butylamine formation fell off much more rapidly with time than it should have if the reaction were of first order with respect to di-*n*-butylamine concentration. The results of run 7 indicate that a nearly complete conversion of di-*n*-butylamine to tri-*n*-butylamine may be obtained when the heating is continued for a considerable period.

(3) (a) Ipatieff, Pines and Schmerling, *J. Org. Chem.*, **5**, 253 (1940); (b) Gilman and Calloway, *THIS JOURNAL*, **55**, 4197 (1933).

(4) Calingaert, Beatty and Soroos, *ibid.*, **62**, 1099 (1940).

TABLE II

THE ACTION OF ALUMINUM CHLORIDE ON DI-*n*-BUTYLAMINE AT THE BOILING POINT

0.252 mole of aluminum chloride added initially per mole of amine.

Run	Reflux period, min.	Composition of reaction products, mole per cent.		
		NH ₃ (C ₄ H ₉)	NH(C ₄ H ₉) ₂	N(C ₄ H ₉) ₃
1	8	4.7	89.4	5.9
2	30	8.5	79.7	11.8
3	60	10.8	73.3	15.9
4	120	16.4	61.1	22.5
5	255	15.8	49.3	34.9
6	360	12.2	45.7	42.1
7	1440	0.5	15.9	83.6

Although the temperature coefficient of the reaction was not determined, it was found that no redistribution occurred at room temperature. Only the starting materials could be isolated from mixtures of aluminum chloride and di-*n*-butylamine which had stood for ten days.

Experiments in Sealed Tubes.—In order to study the reaction further, experiments were conducted in sealed tubes. In this manner the presence of ammonia among the reaction products was shown. For example, upon heating a mixture containing 0.045 mole of aluminum chloride and 0.18 mole of di-*n*-butylamine at 250° for 1800 minutes, the products were found to consist of 20.4, 6.2, 26.8, and 46.6 mole per cent. of ammonia, *n*-butylamine, di-*n*-butylamine and tri-*n*-butylamine, respectively. It was also shown that the same four products could be obtained by heating a mixture of ammonia and tri-*n*-butylamine with aluminum chloride. Thus a mixture made up of 0.040 mole of aluminum chloride, 0.014 mole of ammonia and 0.16 mole of tri-*n*-butylamine was found to consist of 5.6, 1.4, 5.0 and 88.0 mole per cent. of ammonia, *n*-butylamine, di-*n*-butylamine and tri-*n*-butylamine, respectively, after being heated at 250° for 1800 minutes.

In order to obtain a comparison of the reactivity of the *n*-butylamines and the ethylamines, di-*n*-butylamine and diethylamine were mixed separately with aluminum chloride in a mole ratio of 4 to 1 and the mixtures were sealed in tubes. After being heated at 190° for 1440 minutes, the tube to which di-*n*-butylamine had been added was found to contain 29 mole per cent. of tri-*n*-butylamine, while the tube to which diethylamine had been added was found to contain only about 1 mole per cent. of triethylamine. Thus, there is a very large difference in reactivity between the two amines.

Discussion

The mechanism of the reaction reported in this paper probably involves the initial formation of complexes between the amine and the catalyst, in which the metallic atom of the catalyst shares the free pair of electrons of the nitrogen atom. The attachment of the catalyst undoubtedly weakens the other bonds of the nitrogen, giving polarized addition products of the type,

$$R^+ - \overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\text{N}}} : \text{AlCl}_3$$

by the work of Meerwein and co-workers⁵ on complexes between boron trifluoride and alcohols.

These complexes of the structure, $R : \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\text{O}}} : \text{BF}_3$, were not only strong acids, but also good alkylating agents. It should be added that Dougherty⁶ had suggested some time ago that polarized or ionized

intermediates of the type, $\overset{\oplus}{R} - \overset{\ominus}{\text{C}} : \text{AlCl}_3$, were involved in the Friedel-Crafts reaction. It is not considered likely that actual ionization of an alkyl group as a cation occurs in our proposed complexes since there was no indication of rearrangement within a primary alkyl group such as *n*-butyl. According to the views of Whitmore,⁷ a rearrangement to the secondary or tertiary form would be expected if an alkyl cation were formed.

Our work has indicated that the reaction is of second order with respect to aluminum chloride concentration. This suggests that two complexes, such as we have discussed above, are involved in the step during which exchange occurs. In this step a larger complex may be formed which is held together by the ability of each aluminum atom to attain a coordination number of five⁸ by sharing a pair of electrons of a chlorine atom attached to the other aluminum atom. Evidence for the existence of large complexes made up of two molecules of aluminum halide and two organic molecules has been supplied by Kohler⁹ and more recently by Norris and co-workers.¹⁰ Assuming that such complexes are involved, the role of the catalyst is not only to polarize the amine molecules, but also to hold them close enough together so that exchange may occur.

(5) (a) Meerwein, *Ber.*, **66B**, 411 (1933); (b) Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).

(6) Dougherty, *THIS JOURNAL*, **51**, 576 (1929).

(7) Whitmore, *ibid.*, **54**, 3274 (1932).

(8) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 362.

(9) Kohler, *Am. Chem. J.*, **24**, 385 (1900).

(10) (a) Norris and Ingraham, *THIS JOURNAL*, **62**, 1298 (1940); (b) Norris and Wood, *ibid.*, **62**, 1428 (1940).

Experimental

Materials.—The amines were all Eastman Kodak Co. products, and they were carefully fractionated before use. The aluminum chloride, ferric chloride, zinc chloride, and sulfuric acid were anhydrous c. p. products and were used without further purification.

Experiments in Open Vessels.—The catalyst and amine were mixed, with considerable evolution of heat, and the resulting mixture was heated under reflux. In almost every case a two-phase system was obtained. In experiments for which a constant temperature was desired, a large electrically heated oil-bath was used and the solution was frequently shaken. At the end of a definite period the mixture was cooled in an ice-bath and a considerable excess of aqueous sodium hydroxide was added. The amine layer was separated, washed with water, dried over potassium carbonate and finally fractionated.

For large quantities a fractionating column, 40 cm. long, 13 mm. i. d., electrically heated, and packed with glass helices was used. However, many runs were made using only about 30 cc. of solution, and in such cases a Vigreux column, 25 cm. long, and of 8 mm. i. d., was used. The column was very efficient, and, in general, a reflux ratio of 30 to 1 was maintained.

Experiments in Sealed Vessels.—Pyrex bomb tubes were used in this work. Ammonia, if required, was added to mixtures by condensing the gas in the tubes, using a dry ice-alcohol bath. Sealed tubes containing the reactants were heated in an electric furnace. After heating, the tubes were cooled in a dry ice-alcohol bath and then opened. The contents of the tubes were poured into an excess of cold aqueous sodium hydroxide, and the amine layer was separated. The aqueous layer was extracted twice with ether, the ether extracts being added to the

amine layer. The aqueous layer was then distilled into a standard hydrochloric acid solution and the ammonia concentration was determined from the amount neutralized. The amine-ether fraction was dried over potassium carbonate and fractionated, using one of the columns described above.

Preparation of Picrates.—Although the boiling points of the amine fractions indicated that no rearrangements within the alkyl groups had occurred during redistribution, a check was desirable. This was done by preparing the picrates of amine fractions obtained by redistribution. Mixed melting point determinations with picrates prepared from amines obtained from the Eastman Kodak Co. indicated that no changes had taken place within the alkyl groups. The picrates were prepared by mixing 1 g. each of picric acid and the amine and heating until a brown solution was obtained. Six cc. of ethanol was then added and the mixture cooled. The fine yellow crystals which formed were filtered, washed and finally recrystallized from ethanol. The picrates of *n*-butylamine, di-*n*-butylamine and tri-*n*-butylamine melted at 151.59 and 105°, respectively.

Summary

It has been found that when aliphatic amines are heated with metal halide catalysts, the groups attached to the nitrogen are redistributed. This redistribution reaction has been studied with respect to the catalytic activity of several substances and the order of the reaction with respect to catalyst concentration. The mechanism of the reaction has been discussed.

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Some Effects of Solvents upon the Absorption Spectra of Dyes. I. Chiefly Polymethine Dyes

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Introduction

To examine the effect of solvents upon the absorption spectrum of a substance, it is desirable that the spectrum should be measured originally for the substances present as a gas at low pressures and at temperatures comparable with those of the solutions. This is far from easy with dyes, which possess rather large and complicated polyatomic molecules. Low pressures and rather high temperatures are required to volatilize them. Also, they are very liable to decomposition (pyrolysis) with formation of colored (yellow to brown) reaction products.

Experimental

The dyes in which we are primarily interested

are photographically active sensitizing and desensitizing dyes such as cyanines (polymethine dyes), and xanthene and phenazine derivatives. Most of these are salts, and, while it was found possible to volatilize (sublime) a number of them, there was generally too much decomposition for satisfactory spectral measurement. Certain non-saline *merocyanines* first prepared by Brooker¹ could be volatilized at low pressures without contamination. Because of the low pressures necessary, a quite long optical path was used, *viz.*, a 15-ft. tube, operated as an electrical resistance heater furnace by wrapping it with nichrome wire and asbestos (*cf.* Fig. 1).

(1) L. G. S. Brooker, U. S. Patents 2,177,401-2-3.