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Figure 7. The two rings probably do not stand perpendicular to the surface of the metal but, having the same charge, are repelled from each other, forming an angle between them and also with the metal surface, which improves the covering properties of the combined rings.

If the plane of the ring could be made to lie flat in the metal surface, it would give the maximum covering value. p-Phenylenediamine seemed to be the ideal amine to accomplish this end because the two amino groups in para position should draw the ring to the metal surface. Figure 7 shows that this compound is only a moderately good inhibitor; it is about twice as effective as the aniline even if twice the concentration of nitrogen is used, which is necessary to obtain the same number of ions or rings available for adsorption. The ring may actually lie flat in the surface of the metal, but the structure of this compound prevents a close enough packing to make a film which is impenetrable to the hydrogen ions.

Unfortunately many of these nitrogen-containing compounds are only slightly soluble in sulfuric acid so that not enough positive inhibitor ions are formed for complete covering of the metal surface. This is true of diphenylamine-



in which the rings should certainly form a large angle with one and the other, and should therefore have good covering power. With a saturated solution containing 0.00113 per cent nitrogen, this amine gives an effectiveness in reducing corrosion of 16.25 per cent, which is exceptionally high for such a low concentration of the inhibitor. If a solubilizing group can be introduced into this and other slightly soluble amines, they might prove to be excellent inhibitors.

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Amination by Ammonolysis

Effect of Ammonia Concentration

HIS paper represents an extension of earlier studies of the unit process, amination by ammonolysis (3, 4, 5). The report is confined to the influence of ammonia concentration, particularly in those reactions which proceed only to a negligible

extent in the absence of a catalyst. On the basis of experience in the ammonolysis of halogen derivatives of anthraquinones, phenones, keto acids, and

chloronitrobenzene (compounds that can be extensively or completely aminated in the absence of a catalyst, such as copper salts or oxides), the authors had made the following generalizations regarding the benefits to be derived from the use of a more concentrated aqueous ammonia (3): "Amination is more rapid; conversion of reacting aromatic compound to amine is more complete; formation of hydroxy compounds is inhibited; lower reaction temperatures can be used; and,

> The effect of ammonia concentration on the rate of conversion in catalytic ammonolysis depends upon the ammonia ratio, the reaction temperature, and the halogen compound.

> A weaker ammonia gives a higher conversion rate at high ammonia ratios (homogeneous systems), but at low ammonia ratios the reverse is true for 1chloroxenene and 1 - chloronaphthalene, but not for chlorobenzene. When homogeneous systems are employed, there is an increased difference between conver-

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since larger batches can be treated with the same quantity of liquor, economies in the number of pieces of equipment can be effected."

Vorozhtzov and his co-workers of the State Chemical Institute of High Pressures, Leningrad, reviewed the authors' work on this subject (7, 8, 9). With respect to the influence of ammonia concentration, they state (8): "Groggins' assumption to the effect that the rate of reaction of halogen compounds and ammonia increases with the concentration of ammonia has been found to be utterly erroneous for the catalytic process," the determinants being "only the concen-

sion and amination because of concomitant reactions. Such conditions, because they are generally impractical and ignore the penalties which technical operations must suffer when a weak ammonia is used, constitute too small a base for studying the replacement of -Cl by $--NH_{2}$.

Studies on the ammonolysis of pchloronitrobenzene indicate that the influence of ammonia concentration in noncatalytic and catalytic reactions is similar.

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					(16 hours a	t 200° C.)				
Expt. No.	NH₃ Concn.	Aque- ous NH₃	4- Chloro- xenene	Cu (NO ₃) ₂ 3H ₂ O	Catalyst Concn.	Conver- sion, A	Amina- tion, B	100 × Mole Ratio Cu/R·Cl	Mole Ratio NH ₃ / R·Cl	Differenc $A - B$
	%	G r ams	Mole	Mole	G. atom Cu/l.	%	%			
1 2 3 4 5	14 21 28 35 21	304 304 304 292 304	$\frac{1/6}{1/4}$ $\frac{1/3}{2/5}$ $\frac{1/4}{4}$	$\begin{array}{c} 0.03 \\ 0.045 \\ 0.06 \\ 0.072 \\ 0.072 \end{array}$	$\begin{array}{c} 0.0932 \\ 0.1360 \\ 0.1770 \\ 0.2169 \\ 0.2175 \end{array}$	$55.31 \\ 66.20 \\ 86.35 \\ 93.26 \\ 85.56$	$\begin{array}{r} 45.14 \\ 57.68 \\ 80.15 \\ 88.77 \\ 73.82 \end{array}$	$18 \\ 18 \\ 18 \\ 18 \\ 18 \\ 28.8$	$15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\$	10.17 8.52 6.20 4.49 11.74
6 7 8 9 10 11	14 21 28 35 35 21	304 304 304 292 292 304	$\frac{1/6}{1/4}$ $\frac{1/3}{2/5}$ $\frac{1/4}{1/4}$	$\begin{array}{c} 0.02 \\ 0.03 \\ 0.04 \\ 0.048 \\ 0.048 \\ 0.048 \\ 0.048 \end{array}$	$\begin{array}{c} 0.0621 \\ 0.0906 \\ 0.1180 \\ 0.1446 \\ 0.1446 \\ 0.1450 \end{array}$	$\begin{array}{r} 41.20 \\ 58.38 \\ 74.10 \\ 87.02 \\ 98.92 \\ 73.38 \end{array}$	$35.73 \\ 53.44 \\ 71.35 \\ 84.41 \\ 88.99 \\ 64.06$	$12 \\ 12 \\ 12 \\ 12 \\ 19 \\ 2 \\ 19 \\ 2 \\ 19 \\ 2 \\ 19 \\ 2 \\ 19 \\ 2 \\ 19 \\ 2 \\ 19 \\ 2 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 $	$15 \\ 15 \\ 15 \\ 15 \\ 24 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 15 \\ 1$	5.47 4.94 2.75 2.61 9.93 9.32

TABLE I. INFLUENCE OF AMMONIA CONCENTRATION IN PREPARATION OF XENYLAMINE

tration of both chlorobenzene and the catalyst that combine in the complex $C_6H_5Cl \cdot Cu(NH_3)_2^+$, which afterwards reacts with ammonia, hydroxyl ion, and aniline." Furthermore, they concluded that "such a mechanism of the reaction satisfactorily explained the regularities observed not only in the interaction of chlorobenzene and ammonia, but also in the action of ammonia in analogous conditions on other halogen compounds of the aromatic series * * * and that the above suggested mechanism can be generally applied to reactions of the exchange of chlorine in aromatic compounds for an amino group in the presence of copper compounds." Their kinetic studies have been confined to homogeneous reactions, conditions which seldom, if at all, correspond to technical operations. The authors have never made such classical reaction rate studies, nor have they ever reported the results of aminations in homogeneous solution, catalytic or otherwise, and did not, therefore, contemplate such conditions in their quoted generalizations.

In exploring the validity of Vorozhtzov's conclusions, the preparation of xenylamine from 4-chloroxenene (i. e., 4-chlorobiphenyl) was undertaken first because it made possible the isolation of the solid reaction product and the determination of its purity.

The experiments were carried out in the 500-cc. autoclaves used in previous investigations (2). This equipment is not the most suitable for reaction rate studies because a depression of 10° to 12° C. in the oil bath temperature occurs when the autoclaves are immersed, and a time interval of 1 to 1.5 hours is required for a return to the desired reaction temperature. What is more important, however, the experiments do give reliable comparative results for solutions of different ammonia concentrations.

Table I presents two series of experiments with a constant ratio of ammonia and copper to 4-chloroxenene, where the free space in the autoclave is practically the same:

The autoclave contents were filtered on a Büchner funnel, and the residue was dried by suction followed by drying overnight at a temperature below the melting point. The crude xenylamine was titrated against sodium nitrite.

Sodium hydroxide was added to the filtrate which was then evaporated to about 700 cc., cooled, and filtered. Both the residue containing copper oxide and the clear filtrate (made up to 1 liter) were titrated for xenylamine. Chloride was determined gravimetrically on an aliquot portion of the filtrate.

Similar noncatalytic experiments served as a basis for the stated conclusions regarding the practical benefits of a more concentrated ammonia, and these data confirm most of the quoted generalizations. Interesting observations that can be made regarding the yield and purity of the product under the conditions employed are the following: (1) the difference¹

between conversion-i. e., decomposition of halogeno compound as determined by chloride ion, and amination for 18 molar per cent copper is approximately twice as great as that for 12 per cent copper. This is a matter of importance in interpreting the results of subsequent experiments in homogeneous solutions; (2) as the ammonia concentration is increased this "difference" becomes less despite the fact that the reaction has proceeded further; (3) the purity of the crude xenylamine is favored by the use of a more concentrated ammonia solution. Other similar tabulated data for different reaction periods and

also with other copper catalysts and ratios are available and give corresponding results, but are not included here.

In proceeding from heterogeneous to homogeneous reactions -by reducing the quantity of chloroxenene treated with an identical copper-ammonio solution-the data in Table II are obtained. Obviously, such a series of experiments provides a progressively increasing ratio of ammonia and copper to the chloroxenene used. The results show that there is a progressive increase in the per cent conversion as the size of the charge diminishes, but the per cent amination rises to a peak and then drops off. From the data it is apparent that for each copper-ammonio system a roughly constant quantity of halogeno compound enters into reactions not involving the replacement of -Cl by $-NH_2$, and with the reduction in the size of charge, the percentage of these by-products becomes of greater magnitude. Since amination by ammonolysis should concern itself with the replacement of -Cl or other groups by $-NH_2$, it is questionable whether the data for the small charges have any constructive significance in so far as technical operations are concerned, and it is doubtful whether the amination figures beyond the peak have any bearing on amination (not conversion) rates.

TABLE II. INFLUENCE OF COPPER-AMMONIO RATIO IN PREPARATION OF XENYLAMINE

(Time, 20 hours;	temp., 200° C.;	35 per cent aqueous ammonia	= 292 grams)
			AL 1

Expt. No.	4-Chlor	oxenene	Conver- sion, A	Amina- tion, B	100 × Mole Ratio Cu/R·Cl	Mole Ratio NH₃/ R·Cl	Differ- ence, A - B	Chloroxenene Going to Products Other than Xenyl- amine
	Grams	Mole	%	%				Grams
		Cu(N	$O_3)_2 \cdot 3H_2O$	= 2.90 G	rams = 0.0	012 Mol	e	
1 2 3 4 5 6	$75.412 \\ 37.706 \\ 18.853 \\ 11.783 \\ 5.892 \\ 2.946$	0.4 0.2 0.1 0.063 0.031 0.0156	50.77 88.49 94.80 96.43 97.52 98.19	$\begin{array}{r} 46.50 \\ 83.42 \\ 87.72 \\ 81.93 \\ 76.65 \\ 75.69 \end{array}$	3 6 12 19.2 38.4 76.8	15 30 60 96 192 384	$\begin{array}{r} 4.27 \\ 5.07 \\ 7.08 \\ 14.50 \\ 20.87 \\ 22.50 \end{array}$	3.220 1.912 1.335 1.709 1.230 0.663
		Cu(N	$O_{3})_{2} \cdot 3H_{2}O$	= 1.45 G	rams = 0.	006 Mol	e	
7 8 9 10 11	37.706 18.853 9.427 5.892 2.946	${ \begin{smallmatrix} 0.2 \\ 0.1 \\ 0.05 \\ 0.031 \\ 0.0156 \end{smallmatrix} }$	57.84 77.50 82.06 83.34 85.39	52,15 68.16 72.39 66.13 63.27	3 6 12 19.2 38.4	30 60 120 192 384	$5.69 \\ 9.34 \\ 9.67 \\ 17.21 \\ 22.12$	2,145 1.761 0.912 1.014 0.652

When the pertinent data of Table II are plotted with similar data for 28 and 21 per cent ammonia solutions, the curves in Figure 1 are obtained. From the curves and supporting: data the following conclusions can be drawn: (1) With a. decrease in the chloroxenene taken with respect to copperammonio solution, there is a greater difference between conversion and amination; (2) for heterogeneous reactions i. e., with a constant ratio of dissolved chloroxenene to copper-¹ By analogy with aniline, R-OH and R₂NH compounds, but these were not isolated. ammonio solution-the stronger the ammonia solution, the higher is the percentage amination up to the peak; (3) the stronger the ammonia solution, the higher is the peak of percentage amination and the more rapidly is the peak reached; (4) the purity of the product at the peak of amination improves with increased ammonia concentra-

tion. Thus, a more concentrated aqueous ammonia permits the use of larger charges, and makes possible better yields and higher purity of xenylamine.

The conversion curves constantly increase and gradually converge. Because secondary reactions reach such significant proportions, it is

debatable whether the data in this range do not throw more light on concomitant reactions rather than on amination rates.

The fact that the curves for 28 and 21 per cent ammonia solutions, which, despite lower ammonia ratios, intersect and extend above the receding curve for 35 per cent aqueous ammonia, calls for some explanatory comment. It is highly probable that the peak of percentage amination coincides closely with the arrival of homogeneity for each copperammonio system; consequently, it would be more accurate to compare amination rates at or before the peaks only. Because the quantity and percentage of amine formed in the small charge experiments are considerably less than the aminating capacity of the system, and because we have here high ratios of copper to R Cl, which has been shown to cause large differences between conversion and amination, the results indicate merely that dilute ammonia solutions containing much copper are better hydrolyzing agents than more concentrated ammonia solutions. In these homogeneous reactions we must not lose sight of the fact that, with molar ratios of ammonia to R Cl of 100 or 300 to 1, a comparatively large quantity of water is present regardless of the ammonia concentration used, and this fact may also, to some extent, be responsible for differences of approximately 20 per cent between conversion and amination.

Reaction rate studies were next undertaken, and in these experiments it was necessary to provide (1) the same weight of chloro compound, (2) the same ammonia ratio, (3) the same catalyst concentration, and (4) the same freeboard. Since the autoclaves for this work were identical in size and



shape, the freeboard was adjusted by inserting loose-fitting hollow steel cylinders of calculated displacement. The reaction rates of 21, 28, and 35 per cent ammonia solutions were then compared by the following procedure, using a chloroxenene charge of $\frac{1}{3}$ mole:

Concn. NH3	Aqueous NH	NH₃	Vol. Aqueous NH3 at Room Temp.	Cu(NO ₃) ₂ 3H ₂ O	Cu++ per Liter	Disp ment of F	lace- Added e
%	Grams	Grams	Cc.	Grams	G. atom	Grams	Cc.
$21 \\ 28 \\ 35$	$304 \\ 228 \\ 182$	$\begin{array}{c} 63.8 \\ 63.8 \\ 63.7 \end{array}$	$331 \\ 253 \\ 207$	9.665 7.387 6.044	$\begin{array}{c} 0.12085 \\ 0.12085 \\ 0.12085 \\ 0.12085 \end{array}$	600 955	

Because the charge of chloroxenene at the start was probably greater than that required to form a saturated solution, it must be assumed that its concentration was constant, at least during the first part of the run. It would be the same for the various systems only if there were no significant differences in solubility in 21, 28, and 35 per cent aqueous ammonia; but the solubility of the chloro compound, like the respective partial pressures, is an intrinsic property of the ammonia used and there is no satisfactory way of dissociating this factor in comparing the reactivity of the ammonia solutions, nor is such a dissociation desirable.

TABLE III. REACTION RATE STUDIES IN AMINATION OF CHLORO-XENENE Time 5 hours: temperature 200° C : estalvet Cu(NOs): 3Houl

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Expt. No.	Ka	NH₃ Concn. %	4-Chloro- xenene Mole	Cu per Liter (b G. aton	5) Cl- 1 %	Xenyl- amine %	Mole Ratio NH2/4- Chloro- xenene
1 2 3 4 5 b	$\begin{array}{c} 0.01085\\ 0.01379\\ 0.01777\\ 0.01714\\ 0.01508 \end{array}$	21 28 35 35 35	1/10 1/10 1/10 1/10 1/10	$\begin{array}{c} 0.1208\\ 0.1208\\ 0.1208\\ 0.1932\\ 0.1932 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	25.06 30.71 38.72 49.91 48.18	37.5 37.5 37.5 37.5 37.5 37.5
6 7 8	0.00284 0.00339 0.00372	$21 \\ 28 \\ 35$	$\frac{1/3}{1/3}$ $\frac{1/3}{3}$	$\begin{array}{c} 0.1208 \\ 0.1208 \\ 0.1208 \\ 0.1208 \end{array}$	5		$11.25 \\ 11.25 \\ 11.25 \\ 11.25$
a Th	e reaction	rate c	onstant, H	7, was	calculated	from the	expression:
			$K = \frac{1}{bt} \ln t$	$\frac{100}{100-3}$	- x		(1)

for the reaction $C_6H_5Cl + Cu(NH_3)_2^+ \longrightarrow C_6H_5Cl \cdot Cu(NH_3)_2^+$

where b is the concentration of the catalyst in gram atoms/liter, t the time in minutes, x the percentage of chloro compound decomposed = % Cl⁻. Equation 1 was obtained by integration and transformation of the expression for reaction velocity:

$$\frac{dx}{dt} = K (a - x) b \tag{2}$$

Admittedly, the application of these equations to heterogeneous sytems is not valid. Equation 1 has been used only to indicate the relation between reaction rate and catalyst concentration. ^b No Fe cylinder; greater freeboard than other runs of this series by 124 cc.; autoclave volume, 500 cc.

TABLE IV. REACTION RATE STUDIES IN AMINATION OF CHLORO-XENENE

(Time, 5 h chlo	ours; tempe roxenene =	erature, 180 0.1 mole; r	0°C; catal noles NH:/ch	yst, CuCl; loroxenene =	18.853 grams = 37.5)
Expt. No.	K	NH3 Concn.	Cu per Liter (b) G. atom	Cl - %	Xenyl- amine %
1 2 3 4	$\begin{array}{c} 0.00180 \\ 0.00293 \\ 0.00296 \\ 0.00431 \end{array}$	21 28 28 35	$\begin{array}{c} 0.12085 \\ 0.12085 \\ 0.15930 \\ 0.12085 \end{array}$	$\begin{array}{c} 6.31 \\ 10.09 \\ 13.11 \\ 14.48 \end{array}$	3.89 8.55 9.21 10.11

The reaction rate data for the amination of chloroxenene are set forth in Table III. The experiments with both onetenth and one-third molar charges indicate that K varies with the ammonia concentration, and the reaction (conversion) rate is greater for the higher ammonia concentrations.

Experiment 4, using more copper, shows that for the same aqueous ammonia system, K is a function of the catalyst concentration. In this case also the greater difference between conversion and amination, due to increased copper ion concentration, is again in evidence. Experiment 5, in which no cylinder was used, merely confirms the authors' previous experience that both conversion and amination drop off as the free space is increased.

The data in Table IV indicate that cuprous chloride behaves similarly to cupric nitrate, for here again there is convincing evidence that the rate of conversion increases with the ammonia concentration. Owing to the fact that the more dilute ammonia solutions have a much larger volume of liquid to facilitate solution of the halogeno compound and to diminish the concentration of the chloride formed, it is surprising that such favorable results were brought about by increased ammonia concentration.

The ammonolysis of chlorobenzene was next undertaken:

The autoclave contents were transferred to a three-neck flask, sodium hydroxide was added, and the contents were distilled with steam until the distillate no longer gave a test for aniline with potassium bromide-potassium bromate solution and hydrochloric acid. The contents of the flask were filtered, the filtrate was made up to 2 liters, and aliquots were taken for the determination of phenol by Koppeschaar's method and the determination of chloride gravimetrically.

Hydrochloric acid was added to the distillate (acid to Congo Red) and the distillate was distilled with steam. The acid solution remaining was made up to 2 liters and titrated for aniline against sodium nitrite.

The chlorobenzene in the new distillate was separated in a separatory funnel, the aqueous layer extracted with ether, and ether extract added to the chlorobenzene. The liquid was distilled off, finally bringing the temperature to 210° C., when the residue was weighed as diphenylamine (purple color with sulfuric and nitric acid)

The total aniline, phenol, and diphenylamine found agreed with the conversion within 0.5 per cent (0.4 mole charge) and 0.2 per cent (0.8 mole charge).

TABLE V.	REACTION	RATE	STUDIES.	IN	Amination	OF			
CHLOROBENZENE									

(Time, 5 hours; temperature, 180° C.; catalyst, Cu per liter = 0.12085) CuCl; b gram atoms Mole Expt. No. NH_{2} Chloro-Ratic K Concn. Cl-Phenol NH₃/R·Cl benzene Aniline Mole% % % %54.65 53.95 47.22 20.48 19.75 19.32 49.38 48.03 44.00 18.52 17.73 17.75 37.5 37.5 37.5 9.375 9.375 9.375 9.375 $\begin{array}{c} 0.1 \\ 0.1 \\ 0.1 \\ 0.4 \\ 0.4 \\ 0.4 \end{array}$ $\begin{array}{c} 0.02181 \\ 0.02139 \\ 0.01763 \end{array}$ $\begin{array}{r} 4.06 \\ 3.51 \\ 2.83 \\ 1.47 \\ 1.27 \end{array}$ $\frac{1}{2}$

0.00632

0.00607

456

TABLE VI. REACTION RATE STUDIES IN AMINATION OF CHLORO-BENZENE

0.95

(Time, 5 hours grams chlorobe	; temperature inzene = 0.4 b gram ator	e, 180° C.; mole; mole ns Cu per lite	catalyst, Cu(s NH3/chloro r = 0.12085)	$NO_3)_2 \cdot 3H_2O;$ 44.8 benzene = 9.375;
Expt. No.	NH₃ Concn. %	K	C1- %	Aniline %
1 2 3	21 28 35	$\begin{array}{c} 0.00201 \\ 0.00264 \\ 0.00265 \end{array}$	$7.02 \\ 9.14 \\ 9.17$	$6.09 \\ 8.08 \\ 8.31$

The data for reaction rate studies with cuprous chloride as catalyst are given in Table V. For the 0.1-mole charge, 21 per cent aqueous ammonia gives the highest rate and 35 per cent ammonia the lowest. For the 0.4-mole charge the values for conversion and amination are about the same for all of the copper-ammonio solutions. Indeed these particular results bear out the contention of Vorozhtzov that increased ammonia concentration does not increase the reaction rate. When, however, cupric nitrate is used as a catalyst for the 0.4-mole charge (Table VI), the rate of conversion and amination for 28 per cent aqueous ammonia are slightly better than that of 21 per cent ammonia.

Γ_{ABLE}	VII.	INFLUENCE	OF	Temperature	IN	Amination	OF
		Cı	HLOI	ROBENZENE			

(1	1me, 24 ho	urs; ch	loroben	zene =	= 0.1	mo	le; C	uCl =	0.04	mole)	
Expt. No.	K	Temp. ° C.	NH₃ Concn. %	Cu Lite G. a	per r (b) tom		C1- %	Ani	line Z	Mole Ratio NH ₃ / Chloro- benzene	÷
1 2 3 4 5 <i>a</i> 6 <i>a</i> 7 <i>b</i> 8 <i>b</i> , <i>c</i>	$\begin{array}{c} 0.00013\\ 0.00025\\ 0.00172\\ 0.00253\\ 0.02181\\ 0.01916\\ 0.00057\\ 0.00075 \end{array}$	$110 \\ 110 \\ 136 \\ 136 \\ 180 \\ 180 \\ 132 \\ 132 \\ 132$	$21 \\ 35 \\ 21 \\ 35 \\ 21 \\ 35 \\ 21 \\ 35 \\ 21 \\ 35 \\ 35 $	$\begin{array}{c} 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\\ 0.12\end{array}$	2085 2048 2085 2048 2085 2048 2085 2085 2085		2.28 4.29 25.81 35.50 54.65 49.96 9.50 12.19	1. 3. 19. 29. 49. 44. 8. 11.	77 77 86 65 38 13 96 94	37.5 60.0 37.5 60 37.5 60.0 25 25	
a 5 h 5 0.15 0.02	ours. 5 mole chlo 2502 mole	orobenze CuCl i	ene. n 207 d	c. of	35	per	cent	NH3;	955	grams	F

cylinder.

TABLE	VIII.	REACTION	Rate	STUDIES	IN	AMINATION	OF	1-
		CHLC	ORONAP	HTHALEN	E			

(Time, 5 hours; catalyst, CuCl)									
Expt. No.	K Concn. NH %		C1- %	1-Naphthyl- amine %					
Temp. 180° C.; Chloronapht	Chloronaphth halene = 18.7	nalene Taken, 0 5; b Gram Ator	.2 Mole; m Cu per l	Mole Ratio NH_3 liter = 0.12085					
$1 \\ 2 \\ 3 \\ 4$	No catalyst 0.00157 0.00225 0.00249	28 21 28 35	$\begin{array}{c} 0.21 \\ 5.54 \\ 7.84 \\ 8.62 \end{array}$	0 2.32 4.90 5.66					
Temp., 200° C.;	Chloronaphth Chloro	nalene Taken, 0 naphthalene =	.3 Mole; 12.5	Mole Ratio NH ₃ /					
5 6 7 ^a 8 ^a Cu(NO ₃)2·3H	0.00353 0.00430 0.00435 0.00435 0.00430 20 as catalyst.	21 28 28 35	$12.02\\14.43\\14.59\\14.44$	$10.91 \\ 12.38 \\ 12.93 \\ 13.16$					

As was expected, a more concentrated aqueous ammonia gave the higher reaction rates when the operating temperature was lowered to 136° or 110° C. Under these conditions (Table VII) the solubilizing influence of temperature or high ammonia ratios was reduced, while that of ammonia concentration-i. e., higher internal pressure-was accentuated.

Comparing the first four experiments with 5 and 6, the results show that ammonia concentration and ammonia ratio are favorable factors at lower temperatures, but not at 180° C. The last two experiments are of the reaction rate type and show that at lower temperatures the rate of catalytic conversion increases with increase in ammonia concentration.

A final series of catalytic experiments was made on the ammonolysis of 1-chloronaphthalene to 1-naphthylamine:

Autoclave contents were transferred to a three-neck flask, sodium hydroxide was added, and the contents were distilled with steam. The nonvolatile material was cooled and filtered, and the filtrate made up to 2 liters. The distillate, the residue, and an aliquot of the filtrate were titrated for amine, most of the amine being found in the distillate.

In the gravimetric determination of chloride on an aliquot of the filtrate, the silver chloride precipitate was filtered off and dis-solved in aqueous ammonia, then reprecipitated by nitric acid. This served to remove co-precipitated organic matter.

The results in Table VIII show that at 180° C. an increase in conversion and amination rates is brought about by the use of a stronger ammonia. When the reaction temperature is raised to 200° C., the rate for 28 per cent aqueous ammonia is still better than that for 21 per cent aqueous ammonia; but the 35 per cent ammonia no longer has any advantage.

According to Vorozhtzov there is this germane difference between catalytic and noncatalytic ammonolysis: "Whereas the rate of amine formation in noncatalytic change of chloro into amino groups must be directly proportional to the ammonia concentration, this is not true of the catalytic process." To determine the validity of this assumption, a

final series of experiments was run on the noncatalytic ammonolysis *p*-nitrochlorobenzene to *p*-nitroaniline:

Autoclave contents were transferred to a three-neck flask, sodium hydroxide was added, and the contents were distilled with steam. Nonvolatile material was cooled and filtered, and the filtrate made up to 2 liters. The distillate, the residue, and an aliquot of the filtrate were titrated for amine, the residue being nearly pure *p*-nitroaniline. Chloride was determined gravimetrically on an aliquot of the filtrate.

The data in Table IX reveal no pronounced differences whatsoever, for the results show the same trends as in the catalytic ammonolysis of 4-chloroxenene and 1-chloronaphthalene.

TABLE	IX. N	ONCA	TALYTIC	AMMON	OLYSIS	ог р-Сн	LORONITRO-
				BENZENE	3		Mole
Expt No.	Temp. °C.	Time Hr.	NH3 Concn. %	ClC6- H4NO2 Mole	C1- %	p-Nitro- aniline %	Ratio NH3/ ClC6H4NO2
1 2 3 4 5 6	$140 \\ 140 \\ 140 \\ 140 \\ 180 $	4 4 4 4 4	21 35 21 35 21 35	0.4 0.4 0.1 0.1 0.1 0.1	$1.63 \\ 3.52 \\ 4.71 \\ 6.81 \\ 82.73 \\ 91.88$	1.31 3.09 3.64 6.26 78.67 89.16	9.375 9.375 37.5 37.5 37.5 37.5 37.5
8 9 10 11	200 200 200 200 200	4 4 1 1	21 35 21 28 35	$\begin{array}{c} 0.1 \\ 0.1 \\ 0.025 \\ 0.025 \\ 0.025 \\ 0.025 \end{array}$	97.71 98.80 36.19 36.81 36.80	93.47 95.56 31.74 33.98 35.68	37.5 37.5 150.0 150.0 150.0
$12 \\ 13 \\ 14$	$200 \\ 200 \\ 200$	1 1 1	$21 \\ 28 \\ 35 \\ 35 \\ $	$\begin{array}{c} 0.025\ 0.025\ 0.025\ 0.025\ \end{array}$	$36.19 \\ 35.36 \\ 30.12$	$31.74 \\ 32.82 \\ 28.26$	$150.0 \\ 200.0 \\ 240.0$

When the system is heterogeneous at least during a part of the run, the more concentrated ammonia gives the highest rates. When the temperature is elevated and the size of the charge reduced to an utterly impractical $NH_3 : ClC_6H_4NO_2$ ratio of 150 : 1, then the conversion rates become practically identical, although the degree of amination is still favored by increased ammonia concentration. Working with the same volume of ammonia liquor (by omitting the steel cylinders) and thereby further increasing the ammonia ratio, experiments 12 to 14, inclusive, show that the most concentrated ammonia gives the poorest results. Exactly such a phenomenon was observed in the similar treatment of chloroxenene (Figure 1).

Discussion²

AMMONIA CONCENTRATION. It can be predicted that the solubility of sparsely soluble halogeno compounds will vary for each ammonia concentration. As is evidenced by the slope and peaks of the curves of Figure 1, each system will arrive at homogeneity at different ammonia liquor ratios. If conditions are to be chosen to compare diverse ammonia systems, it should be remembered that a more concentrated ammonia is employed to yield the specific technical advantages previously set forth. When comparisons are made at comparatively high temperatures or with excessive ammonia ratios, the advantageous properties of concentrated ammonia are obliterated; consequently, the conclusions drawn from reaction rate studies in homogeneous systems ignore the penalty we must pay for employing weak ammonia. Disregarding all practical considerations, there is reason to doubt the conclusions which may be drawn by applying a single reaction-rate expression in the comparison of different ammoniacal solutions. The curves and tabulated data show that the relation of ammonia concentration to amination and conversion for both catalytic and noncatalytic reactions is significantly altered by changes in temperature and ammonia liquor ratio.

^a By P. H. Groggins.

TYPE OF COPPER CATALYST. There appears to be little doubt that for any particular ammonia concentration, within limits, the rate of conversion is a function of the copper concentration. The anion accompanying the copper is not, however, without influence since the introduction of hydroxyl or nitrate ions also influences the known reactions. The fact that cupric nitrate serves as well as cuprous salts in some aminations indicates that the conclusions of Vorozhtzov (7, 8) that "compounds of univalent copper are more active as catalysts as compared with compounds of bivalent copper," although valid for the amination of chlorobenzene, cannot be generalized.

The technical and patent literature contains many references extolling the advantages of cuprous compounds, whereas some of the data here (Table VIII) and also in the previous investigation relating to the preparation of 2-aminoanthraquinone (5) indicate that cupric compounds are equally serviceable. The more favorable action of cuprous salts in the preparation of aniline and p-phenylenediamine may be explained by assuming: (1) Chlorobenzene and p-dichlorobenzene behave differently from chloroxenene or chloroanthraquinone; (2) the cupric salt used in the ammonolysis of chloroxenene and chloronaphthalene, etc., is reduced; or (3) certain amines (e. g., aniline) when formed are readily susceptible to oxidation by the anion of the cupric salt. The concentration of copper for the conversion of chlorobenzene is consequently reduced because some of it enters into the second catalytic reaction-viz., the oxidation of aniline.

While not challenging the validity of any of the other hypotheses, certain lines of evidence are presented in support of the oxidation theory: (1) Cupric and cuprous compounds are about equally active in the preparation of amines which are not readily susceptible to oxidation; (2) in the preparation of easily oxidizable amines, a low catalyst concentration results in a smaller difference in the reaction rates when cuprous and cupric compounds are compared; (3) the treatment of aniline with cupric nitrate leads to a much greater oxidation of amine than with cuprous chloride. The introduction of potassium chlorate markedly accelerates this reaction. Here, as in the problem of reaction rates, the temperature of reaction plays an important role and the data do not permit of broad generalizations. The preceding observations do, however, explain why oxidants may be used in the preparation of aminoanthraquinone and must be avoided in the preparation of aniline.

INFLUENCE OF AMMONIUM CHLORIDE. This discussion relates largely to that segment of ammonolysis involving the final 5 to 10 per cent of the following reaction:

$R \cdot Cl + 2NH_3 \longrightarrow R \cdot NH_2 + NH_4Cl$

The reaction has now slowed down markedly, and either a higher temperature or relatively long period of time is required for completion. These instrumentalities will undoubtedly effect the decomposition of the halogeno compound, but data are available to show that in the preparation of certain solid amines neither the yield nor purity is commensurately improved. The net result is a substantial conversion to products other than amine. By analogy with esterification, etc., it appeared logical that the reaction could be favorably completed by removing one of the products of reaction (viz., ammonium chloride).

As a result of previous studies (3), the writers concluded that "the pH of aqueous ammonia decreases with rising temperature and more rapidly under such conditions when ammonium salts were introduced." They also discovered in their amination of 2-chloroanthraquinone that "oxidation (with chlorates) was found to be the most satisfactory method of counteracting the influence of hydrochloric acid or its ammonium salts in the reaction mass," and concluded "the

efficiency of potassium chlorate may probably be accounted for by the following reactions:

$$6\mathrm{R}\cdot\mathrm{NH_3}^+ + 6\mathrm{Cl}^- + \mathrm{KClO_3} \longrightarrow 6\mathrm{R}\cdot\mathrm{NH_2} + \mathrm{KCl} + 3\mathrm{H_2O} + 3\mathrm{Cl_2}$$

"The preceding representation indicates that there will be a temporary diminution of the hydrogen-ion concentration because of the formation of un-ionized water as a result of oxidation* * * It is also known that in the absence of acidity, potassium chlorate in aqueous solution would not exert the oxidizing effect which takes place. The decomposition of chlorate depends, therefore, on the presence and reaction with hydrogen ions."

Regarding these conclusions Vorozhtzov states: "The explanations given by Groggins for the favorable action of potassium chlorate and other oxidizing agents is incorrect. The reaction mass is alkaline and, therefore, hydrochloric acid which is present as ammonium chloride should not react with potassium chlorate. (The reaction velocity of hydrochloric acid with potassium chlorate is directly proportional to the cube of the hydrogen-ion concentration.) The favorable action of oxidizing agents should rather be attributed to the fact that they oxidize the reduced β -aminoanthraquinone and by doing so improve its quality, or to the fact that they oxidize ferrous ions to ferric and thus prevent the reducing of β -aminoanthraquinone."

Unfortunately, no experimental data are presented by Vorozhtzov which might throw light on this subject and which, admittedly, is a fruitful line of research. The reference to the hydrogen-ion concentration necessary to decompose potassium chlorate is hardly germane to aminations carried out in iron autoclaves. His explanation involving the oxidation of reduced anthraquinone is unlikely and contradictory because it presumes that the chlorate is first inactive and then active and does not account for its decomposition. The important fact is that, under the optimum conditions previously reported (5), the chlorate does react and disappears almost completely. Furthermore, Vorozhtzov's admission that the chlorate is decomposed and that an oxidation actually takes place rather confirms and strengthens the authors' hypothesis: The decomposition of chlorate depends on the presence and reaction with hydrogen ions. The fate of the chlorine in the suggested mechanism of reaction is not definitely known. It may (1) directly or indirectly oxidize the iron surfaces of the autoclave, and (2) oxidize some of the amine, evidence of which is generally obtainable and frequently apparent.

Experiments conforming to optimum operating conditions show that there is 6.5 per cent decomposition of the chlorate when the autoclave contains only aqueous ammonia, potassium chlorate, and ammonium chloride, but when 2-chloroanthraquinone is also present, there is a virtual disappearance of chlorate on completion of a 20-hour run at 200° C. Similar experiments in open flasks reveal that the percentage of chlorate decomposition is approximately six times as great for aqueous solutions of ammonium chloride plus potassium chlorate plus iron as for corresponding ammoniacal solutions. It is thus apparent that chlorate reacts appreciably only when an oxidizable compound—e.g., iron or aniline—is present. Furthermore, it is probable that this decomposition of chlorate occurs in a neutral or acid medium, or on surfaces covered with hydrogen or ammonium ions.

Calcott (1) found that "certain acid inhibitors of the type pyridine, quinoline, and thiocarbanilide, etc., also produce similar beneficial results" in ammonolysis and has concluded that "apparently any material which strongly inhibits the solution of iron under the conditions existing in amination, would also improve yield and quality of product." The theories relating to the efficacy of acid inhibitors are ably summarized by Mann and co-workers (6). It is generally agreed that inhibitor molecules reduce the rate of discharge of hydrogen on the cathodic areas of iron and thus inhibit its solution. Why acid inhibitors are useful if the charge is alkaline, as Vorozhtzov contends, is a subject for study and speculation.

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Composition of Petroleum Wax

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THE composition of wax from petroleum or allied substances has been the subject of many investigations. That such wax generally contains a large percentage of normal paraffin hydrocarbons seems to be well established. Francis, Watkins, and Wallington (β) , for example, found that twenty-one fractional distillations of wax from a Scotch shale oil separated it into constant-boiling fractions. Piper, Brown, and Dyment (6) measured with x-rays the "spacings" of Francis' wax fractions and found that they agreed with those of the synthetic normal paraffins. They concluded that these fractions were composed of hydrocarbons identical in constitution with the normal paraffins.

However, in addition to fractions composed of normal

paraffins, several investigators have obtained wax fractions. the melting points of which were far below those of the normal paraffins and which consequently were not composed of a mixture of normal paraffins.

By fractional crystallization from ethylene chloride of narrow-distillation cuts of wax from a Midcontinent petroleum, Ferris, Cowles, and Henderson (2) obtained several series of fractions; each series was composed of fractions of substantially the same molecular weight and boiling point. These investigators concluded that the more insoluble fractions were made up of normal paraffins, since their melting points and refractive indices agreed closely with those for synthetic normal paraffins. The melting points of the more soluble fractions were, however, about 30° C. lower than those