[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

THE ACTION OF BASES ON ORGANIC HALOGEN COMPOUNDS. II. BASIC CATALYSIS IN THE DEHALOGENATION OF THE PHENYL HALIDES*

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The authors, with Chandler and Gilkey, have shown in the preceding paper[1] that potassium amide reacts rapidly with chlorobenzene, bromobenzene and iodobenzene in liquid ammonia solution at −33° to give aniline and diphenylamine, together with smaller amounts of triphenylamine and *p*-aminobiphenyl. The present paper reports experiments designed to afford an explanation of the formation of the three last-named products.

It is known from the work of White, Morrison and Anderson[2] and Eatough[3] that the reactions expressed by the equations,

$$C_6H_5NHK + C_6H_5X = (C_6H_5)_2NH + KX \tag{1}$$

$$(C_6H_5)_2NK + C_6H_5X = (C_6H_5)_3N + KX \tag{2}$$

do not take place in liquid ammonia at −33°, a conclusion that we have verified. However, a fair yield of diphenylamine may be obtained by adding potassium amide to a solution of potassium anilide and chlorobenzene, and of triphenylamine by adding potassium amide to a solution of potassium diphenylamide and chlorobenzene, both reactions being carried out in liquid ammonia at −33°. Since the yields are much better than that obtained by treating chlorobenzene with potassium amide alone, one must conclude that the amide ion, NH_2^-, catalyzes the reactions of equations (1) and (2), although the mechanism by which this is accomplished is at present not definitely known.†

That such a catalysis occurs is shown also by determining the halide

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* From the Ph.D. Thesis of Richard E. Wright, October, 1935.

[1] BERGSTROM, WRIGHT, CHANDLER AND GILKEY, THIS JOURNAL, **1**, 170–178 (1936).

[2] WHITE, MORRISON AND ANDERSON, *J. Am. Chem. Soc.*, **46**, 967 (1924).

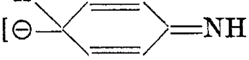
[3] EATOUGH, *Thesis*, Brown University, **1927**.

† It is assumed, in using the term "catalysis," that reactions (1) and (2) proceed normally at an extremely slow rate in the absence of NH_2^-.

ion formed in reactions where potassium amide is added to a mixture of phenyl halide and potassium anilide (or potassium diphenylamide) in liquid ammonia. Yields of 70–90% of halide ion, calculated from the equation

$$C_6H_5X + KNH_2 = C_6H_5NH_2 + KX \tag{3}$$

are obtained, whereas, when potassium amide is added to a phenyl halide alone, the yield of halide ion is only 50–60% of the theoretical, the remainder having therefore been formed in the reactions of equations (1) and (2). [Yield of halide ion = (100 × equivalents halide ion)/(atoms K used).]

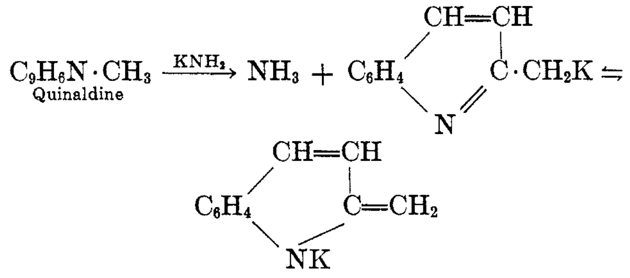
p-Aminobiphenyl is possibly formed from a phenyl halide and a p-quinoid form of potassium anilide, K^+[], in the presence of NH_2^- ions.

The catalytic effect of the amide ion may be demonstrated for a number of reactions of the type,

$$C_6H_5Cl + K{\cdot}R \xrightarrow{NH_2^-} C_6H_5{\cdot}R + KCl \tag{4}$$

when R·H is a sufficiently weak "acid" in liquid ammonia. Thus, quinaldyl potassium, which will not alone react with chlorobenzene[4] in liquid ammonia solution at −33°, does so when potassium amide is added, to give 2-benzylquinoline, 2-benzohydrylquinoline (?), and 2-triphenylmethylquinoline (?). The following equations express the reactions.

(5)



$$C_9H_6N{\cdot}CH_2K + C_6H_5Cl \xrightarrow{NH_2^-} C_9H_6N{\cdot}CH_2C_6H_5 + KCl \tag{6}$$

$$C_9H_6N{\cdot}CH_2C_6H_5 + KNH_2 = C_9H_6N{\cdot}CHKC_6H_5 + NH_3 \tag{7}$$

$$\text{or, } C_9H_6N{\cdot}CH_2C_6H_5 + C_9H_6N{\cdot}CH_2K \rightleftharpoons C_9H_6N{\cdot}CHKC_6H_5 + C_9H_6N{\cdot}CH_3$$

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[4] BERGSTROM, *J. Am. Chem. Soc.*, **53**, 3034 (1931).

(8) $C_9H_6N\cdot CHKC_6H_5 + C_6H_5Cl \xrightarrow{NH_2^-} C_9H_6N\cdot CH(C_6H_5)_2 + KCl$

(9) $C_9H_6N\cdot CH(C_6H_5)_2 \xrightarrow{KNH_2} C_9H_6N\cdot CK(C_6H_5)_2 \xrightarrow[NH_2^-]{C_6H_5Cl} C_9H_6N\cdot C(C_6H_5)_3$

Triphenylmethylpotassium, which reacts very slowly with chlorobenzene in liquid ammonia at −33°, reacts much more rapidly in the presence of potassium amide to give a 46% yield of tetraphenylmethane—the best that has so far been obtained by any reaction.

(10) $(C_6H_5)_3C\cdot K + C_6H_5Cl \xrightarrow{NH_2^-} (C_6H_5)_4C + KCl$

On the other hand, potassium phenoxide, the salt of an acid stronger than any of those treated above, does not appear to react with chlorobenzene or bromobenzene, even in the presence of potassium amide. The following reaction, involving the salt of a very strong acid, does not take place, although bromobenzene is twenty times as reactive toward potassium amide as is chlorobenzene.[1]

(11) $C_6H_5Br + KCl \xrightarrow{NH_2^-} C_6H_5Cl + KBr$

Preliminary experiments indicate that diphenylmethylpotassium, which reacts slowly with chlorobenzene to give triphenylmethane and tetraphenylmethane, catalyzes the formation of triphenylamine according to the reaction of equation (2). There is, however, indication that diphenylmethylpotassium may be slightly ammonolyzed at room temperatures in liquid ammonia, and the possibility remains that these results are occasioned in part by a low concentration of amide ions, rather than by diphenylmethyl ions exclusively. Thus

(12) $$(C_6H_5)_2CH^- + NH_3 \rightleftharpoons (C_6H_5)_2CH_2 + NH_2^-$$

DISCUSSION

Because of the lack of experimental proof, we shall for the present forego an extended discussion of the mechanisms of the reactions treated in this paper, satisfying ourselves with a few generalizations from the point of view of Brønsted's theory of acids and bases. It will be recalled that Brønsted[5] defined an acid as any substance regardless of charge which can, under the conditions of the reaction, yield a proton, and a base as any substance which can accept a proton. Therefore, all of the anions which have been found in the present work to replace aromatically bound halogen may in this sense be regarded as bases. These may be arranged in a series of decreasing reactivity toward the phenyl halides.

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[5] BRØNSTED, *Chem. Rev.*, **5**, 231 *ff.* (1928).

Base	NH_2^-	$(C_6H_5)_2CH^-$	$(C_6H_5)_3C^-$	$C_6H_5NH^-$	$(C_6H_5)_2N^-$	$C_6H_5O^-$
Rate of reaction with C_6H_5X in NH_3.....	rapid	slow	slow	do not react at −33°		
Activity as a catalyst in NH_3............	high	slight	?	?	?	?
		React with C_6H_5X in the presence of NH_2^-				Does not react with $C_6H_5X + NH_2^-$

The position of the quinaldyl ion is unknown. The relative activities of the anions are, at least qualitatively, directly related to their strengths as bases in the above sense, or to their proton affinities.[6] Catalytic activity is shown definitely by the strongest base (NH_2^-) and probably to a lesser extent by the diphenylmethyl anion. It is reasonable to assume that all bases approaching or exceeding the amide ion in strength will be active as catalysts. Possibly the almost exclusive formation of triphenylamine in the reaction of the phenyl halides with sodium in liquid ammonia[7] is connected with the catalytic activity of the negative electron, which is present in solutions of the alkali metals.[8]

EXPERIMENTAL

The technique for carrying out reactions in liquid ammonia, for the determination of halide ion, and for the separation of aniline from diphenylamine has been described in the first article of this series.[1] All organic compounds used in the present work, although supplied by the Eastman Kodak Company, Kahlbaum, or the Gesellschaft für Teerverwertung in a state of high commercial purity, were fractionated, the middle fractions being retained.

Potassium anilide and phenyl chloride.—Potassium amide was made in vessel *1*, and transferred quantitatively to vessel *2* by the method of the previous article.[1] Slightly more than one equivalent of aniline was introduced into *2* from a weighing pipet, followed after the lapse of five or ten minutes by chlorobenzene, the reaction mixture being stirred mechanically throughout. Solvent was evaporated from the reaction vessel during the next two to three hours. Benzene was added, and hydrolysis was effected by the slow addition of water. Chloride ion was determined in the combined aqueous extracts of the benzene layer.

(Two expts.) Atoms K, 0.02085, 0.01595; moles $C_6H_5NH_2$, 0.02414, 0.02194; moles C_6H_5Cl, 0.0204, 0.0171; Cl^-, 3.7%, 0.8%, calculated on the basis of potassium [equation (1)]. It is thought that the chloride ion results in part, at least, from the reaction between chlorobenzene and potassium amide which has spattered on the walls of vessel *2* above the liquid level.

Potassium diphenylamide and phenyl chloride.—The reactions were carried out

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[6] BENNET, *Annual Reports on the Progress of Chemistry*, **26**, 136 (1929), has stressed the importance of the proton affinity of the reagent in reactions involving the replacement of halogen in substituted phenyl halides.

[7] WHITE, *J. Am. Chem. Soc.*, **45**, 779 (1923).

[8] KRAUS, *ibid.*, **43**, 749–70 (1921), and previous articles.

as described in the preceding paragraph, except that diphenylamine was used in place of aniline. In the third run especial pains were taken to avoid spattering of the potassium amide solution.

ATOMS K	MOLES $(C_6H_5)_2NH$	MOLES C_6H_5Cl	CHLORIDE ION (%)
0.01402	0.02373	0.0165	2.2
0.0130	0.0163	0.0193	1.3
0.01846	0.01843	excess	0.6

Chloride ion was calculated on the basis of the potassium [see equation (2)].

The Catalytic Effect of the Amide Ion: Chlorobenzene, potassium anilide (or diphenylamide) and NH_2^-.—The description of a typical run follows. 100 cc. of liquid ammonia was condensed in vessel *1*, as previously described,[1] a weighed amount of potassium was introduced in a broken glass capsule, and converted to amide by the catalytic action of clean iron wire (Table I, column 1). The solution was transferred quantitatively to vessel *2*, the last portions being washed over with fresh solvent. To this was added an approximately equivalent amount of aniline or diphenylamine, with vigorous mechanical stirring, the chlorobenzene being introduced after five or ten minutes. With the stopcock connecting the two containers closed, another 100 cc. of liquid ammonia was condensed in *1*, and potassium was introduced in weighed amount, this being converted to amide under the influence of the iron wire already in the vessel (Table I, column 2). The potassium amide in vessel *1* was slowly siphoned over into vessel *2*, with continuous stirring. A rapid reaction ensued, with the formation of an opaque reddish-brown solution. After the lapse of ten or fifteen minutes, the reaction vessel was removed from the insulating Dewar to hasten the evaporation of the ammonia, which generally consumed two or three hours. The solvent-free residue was worked up and reaction products were determined in the manner described in the first article.

From the preceding article[1] it is known that a 53-58% yield of chloride ion is obtained when potassium amide is added to an excess of chlorobenzene in liquid ammonia. The yields of chloride ion in Table I, calculated on the basis of the same equation, are much higher, indicating that the potassium anilide or potassium diphenylamide is taking part in the reaction, thus demonstrating the catalytic effect of the amide ion. The results further show that *p*-aminobiphenyl is formed from potassium anilide, and that the reaction,

$$(C_6H_5)_2N^- + NH_2^- \rightleftharpoons 2C_6H_5NH^- \qquad (13)$$

does not occur, for otherwise the yields of aniline (column 7, last two entries) would be much greater.

Quinaldylpotassium, chlorobenzene and potassium amide.—Quinaldine, (0.0196 mole), was added to 0.0304 mole of potassium amide in 100 cc. of ammonia in vessel *2*, followed in a few moments by 0.0476 mole of chlorobenzene. To this deep-red mixture was added 0.0257 mole of potassium amide, which had been prepared in vessel *1*. Solvent was evaporated during the next three hours, and the mixture was hydrolyzed after it had first been covered with a layer of benzene. The benzene solution, after successive extractions with water, dilute hydrochloric acid and 18 *N* sulfuric acid, was evaporated to dryness under reduced pressure, leaving a solid (Solid II), which melted at 190.5-191.5° uncorr. after crystallization from alcohol.

A viscous tar separated when the benzene solution was extracted with hydrochloric acid. The petroleum ether extract of the tar was evaporated, and the solid formed was treated with cold alcohol, to dissolve most of the tar. After filtration, the white, solid residue was crystallized from 80% alcohol; m.p., 110.5–112.0°, uncorr. (Solid I). The hydrochloric-acid-soluble portion was brought to the methyl red endpoint with dilute sodium hydroxide and extracted with benzene. The benzene solution was distilled to remove solvent, then distilled under reduced pressure (about 20 mm.), quinaldine first passing over, followed by a dark viscous oil at 210–

TABLE I

VESSEL *1*		VESSEL *2*		YIELDS				
Atoms K	Atoms K	Moles Amine	Moles C_6H_5Cl	Cl^{-b}	$PhNH_2$	Ph_2NH^a	$Ph_3N^{a,c}$	p-$C_6H_5C_6H_4NH_2^g$
				%	*% Recovered*	*% Theoretical*		%
0.04109	0.02849	0.03811 $PhNH_2$	0.060	78.2	70.5[d]	57.0	present	5.9
0.04114	0.02886	0.04741 $PhNH_2$	0.062	75.5	68.0[d]	58.4	present	7.1
					% Theoretical	*% Recovered*		
0.03644	0.03435	0.03178 Ph_2NH	0.0518	85.6	20.9	77[f]	79	trace
0.03673	0.03299	0.03312 Ph_2NH	0.0518	89.4	21.2[e]	78[f]	59	trace

(*a*) Theoretical yield of di- or triphenylamine = 100 (moles amine obtained)/(total atoms K in both vessels minus moles aniline or diphenylamine, column 3). The aniline or diphenylamine in II reacts with an equivalent of KNH_2. The equations, $2\ C_6H_5Cl + KNH_2 = (C_6H_5)_2NH + NH_3 + 2KCl$ and $3C_6H_5Cl + 3KNH_2 = (C_6H_5)_3N + 3KCl + 2NH_3$ have been assumed, but since the yields of amines total over 100% in one experiment (#3) it is evident that potassium anilide, C_6H_5NHK, or potassium diphenylamide, $(C_6H_5)_2NK$, are not inert, but react with the chlorobenzene in the presence of NH_2^-.

(*b*) The chloride ion was determined as silver chloride in the aqueous part of the hydrolysate of the reaction mixture. The yield of chloride ion was calculated on the basis of the potassium amide in excess of an equivalent amount of amine, assuming the reaction, $C_6H_5Cl + KNH_2 = C_6H_5NH_2 + KCl$. Yield $Cl^- = 100$ [equivalents Cl^-/atoms K (column 1)].

(*c*) Crude; m.p., after cryst. from alc., 124–5°; m.p. of mixture with authentic triphenylamine the same. A small amount of triphenylamine could not be separated from another solid with which it formed a mixture melting at about 118–9°. A portion of the triphenylamine in experiment 4 was lost.

(*d*) Expressed as per cent. of the aniline in column 3.

(*e*) Expressed as the per cent. of the theoretical aniline, assuming the equation, $C_6H_5Cl + KNH_2 = C_6H_5NH_2 + KCl$, and calculated on the basis of the potassium in excess of the amount necessary to form potassium diphenylamide. Moles $C_6H_5NH_2$, theoretical = total atoms K (columns 1 + 2) minus moles Ph_2NH (column 3).

(*f*) Expressed as per cent. of the diphenylamine in column 3.

(*g*) Theoretical yield of p-aminobiphenyl, in mols = 1/2 (total atoms K, columns 1 and 2, minus moles aniline) × 169.1. [Mol. wt. p-$C_6H_5C_6H_4NH_2 = 169.1$.]

280°. This was converted in alcoholic solution to a picrate; m.p., 155–6°. M.p. of mixture with the picrate of 2-benzylquinoline, 155–6°.[9] In the reaction a chloride ion yield of 93.3% of the theoretical was obtained, indicating again the catalytic effect of the NH_2^- ion. [*Cf.* note (*b*), Table I.]

In a repetition of this run, ammonium bromide was added to the ammonia solution to destroy reactive potassium salts and minimize the formation of tar. Yield: 2.01 g. Solid I (0.0068 mole); 0.97 g. Solid II (0.0026 mole); and some 2-benzylquinoline. (Starting with 0.038 mole KNH_2 in vessel *1*, 0.0293 mole quinaldine and 0.132 mole chlorobenzene in vessel *2*, and an additional 0.077 mole KNH_2 in vessel *1*.)

Mol. Wts.—Solid I: Solute (g.), 0.2784, 0.2001; C_6H_6 (g.), 17.23, 17.23; lowering of f.p., 0.280°, 0.200°. Mol. wt. found, 283, 284. Calc'd for $C_{22}H_{17}N$, 295. *Solid* II: Solute (g.), 0.2857, 0.2443; C_6H_6 (g.), 19.82, 19.81; lowering of f.p. 0.182°, 0.160°. Mol. wt. found, 388, 378. Calc'd for $C_{28}H_{21}N$, 371.

Anal. Solid I Found: C, 89.43; H, 5.78; N, 4.96.

Calc'd for $C_{22}H_{17}N$ (2-benzohydrylquinoline): C, 89.44; H, 5.81; N, 4.75.

Solid II Found: C, 90.13; H, 6.03; N, 4.52.

Calc'd for $C_{28}H_{21}N$: C, 90.5; H, 5.7; N, 3.8. The analysis is unsatisfactory, but indicates 2-triphenylmethylquinoline.

Potassium amide, potassium phenolate and chlorobenzene.—Potassium amide, in vessel *1*, was added to a solution of potassium phenolate (prepared from potassium amide and phenol) and an equivalent of chlorobenzene in vessel *2*. Following the customary treatment, attempts were made to isolate diphenyl ether from the hydrolysate, but without success, although the small residue left after evaporation of the benzene extract had an odor like that of the expected compound. Two experiments gave the following results. Atoms K, 0.0319, 0.0424; moles phenol, 0.0183, 0.0252; moles C_6H_5Cl, 0.052, 0.054; yield of halide ion (theoretical yield in equivalents = atoms of K minus moles of phenol) = 55.9%, 58.6%; yield of aniline, 31.2%, 29.8% [see Table I, note (*e*)]; yield of diphenylamine, 7.8%, 11.4%.

Since approximately a 55% yield of chloride ion is obtained by adding potassium amide to an excess of chlorobenzene in ammonia[1] it may be concluded that potassium phenolate and chlorobenzene do not react appreciably in the presence of amide ions.

A portion of the aniline could result from the reaction,

$$(C_6H_5)_2O + 2KNH_2 = C_6H_5OK + C_6H_5NHK + NH_3, \tag{14}$$

but this was found not to proceed at a measurable rate under the present experimental conditions.

Potassium triphenylmethyl, chlorobenzene and potassium amide.—Triphenylmethane (0.0241 mole) was added to potassium amide (0.0296 mole) in vessel *2*, followed after an hour by chlorobenzene (0.0714 mole). To this mixture was added potassium amide (0.0420 mole) solution from vessel *1*, the solvent being slowly evaporated over a period of about 3 hours. The hydrolysate was extracted several times with benzene, and this in turn was extracted with dilute hydrochloric acid to remove amines. The benzene solution was evaporated, and the residue was crystallized from the same solvent; m.p., 277–8° uncorr. M.p. of mixture with known tetraphenylmethane,[10] 277–8°, showing their identity.

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[9] Prepared by the method of Bergmann and Rosenthal, *Jour. prakt. Chem.*, **135**, 275 (1932).

[10] Prepared by the method of Kraus and Kawamura, *J. Am. Chem. Soc.*, **45**, 2760 (1923).

Aniline, 13.9%, calculated on basis of KNH_2 in excess of the quantity equivalent to the $(C_6H_5)_3CH$. Diphenylamine, 20%, calculated as above. Tetraphenylmethane, calculated on basis of $(C_6H_5)_3CH$, 46% (3.53 g.).

Potassium triphenylmethyl and chlorobenzene.—Potassium triphenylmethyl was prepared in vessel *2* by adding triphenylmethane to two equivalents of potassium amide (from potassium solution and iron wire). To this was added an excess of phenyl chloride, the solution standing for one hour, three hours more being required for the forced evaporation of the solvent. Tetraphenylmethane was isolated and identified, although not determined quantitatively, in the benzene extract of the hydrolysate. Since aniline was not found among the reaction products, it may be concluded that triphenylmethylpotassium is not appreciably ammonolyzed to potassium amide and triphenylmethane under the experimental conditions.

Atoms of K, 0.02430; mole $(C_6H_5)_3CH$, 0.02398; mole C_6H_5Cl, 0.029; chloride ion, 28.5% of theoretical; aniline, none.

TABLE II

K ATOM	$(C_6H_5)_2CH_2$ MOLE	C_6H_5Cl MOLE	Cl^-, % THEORETICAL	$C_6H_5NH_2$, % THEORETICAL	DURATION OF RUN
0.02567	0.02514	0.052	84.7	0.5	2 hrs.
0.01361	0.01372	0.0174	40.3	1.9	6 hrs.

TABLE III

K ATOM	$(C_6H_5)_2CH_2$ MOLE	$(C_6H_5)_2NH$ MOLE	Cl^{-a} %	ANILINE[b] %	$(C_6H_5)_2NH$ RECOVERED	$(C_6H_5)_3N$ %
0.02342	0.01146	0.01160	111	1.1	61%	39
0.03273	0.01626	0.01592	63	2.8	86	10

(*a*) Calculated on the basis of the potassium in excess of the amount required to form $(C_6H_5)_2N\cdot K$.

(*b*) Calculated on the basis of the potassium. ($1K \Bumpeq 1C_6H_5NH_2$.)

Potassium diphenylmethyl and phenyl chloride.—Potassium diphenylmethyl was prepared from potassium amide and diphenylmethane, and treated with chlorobenzene, in the manner of the preceding experiment. The results appear to depend upon the purity of the diphenylmethane, which, for the first runs (both tables), was redistilled Eastman material, boiling range 2°, and for the second run the same, distilled again, boiling range, 1.5°.

Triphenylmethane and tetraphenylmethane were not determined quantitatively but were isolated and identified in the benzene extract of the hydrolysate. (The benzene had been extracted with dilute HCl to remove amines.)

In the following runs, a mixture of diphenylmethane and diphenylamine was added to potassium amide in vessel *2*; then phenyl chloride was introduced. Duration of runs, 5.5–7 hours. Mole C_6H_5Cl, 0.0568 in first run; an excess in the second. $\%Cl^- = 100 \times [Cl^- \text{obtained}/(\text{atoms K} - \text{moles } (C_6H_5)_2NH)]$. Yield of $(C_6H_5)_3N = 100 \times [\text{moles } (C_6H_5)_3N/\text{moles } (C_6H_5)_2NH \text{ used}]$. M.p. $(C_6H_5)_3N$, cryst. alc., 123–4°.

Tetraphenylmethane and triphenylmethane were also identified as reaction products. The small quantities of aniline reported are doubtless formed by the action of potassium amide on chlorobenzene. The potassium amide may have been left in slight excess because of imperfect introduction of the diphenylmethane and diphenylamine, or it may have been formed by ammonolysis of the diphenylmethylpotassium.

Since the yields of chloride ion are higher than that obtained when chlorobenzene reacts with potassium amide alone,[1] and since considerable triphenylamine is formed, it is evident that potassium diphenylamine and phenyl chloride are reacting under the catalytic influence of the diphenylmethyl ion. It may of course be argued that amide ions, formed in accordance with the equation,

$$(C_6H_5)_2CHK + NH_3 \rightleftharpoons (C_6H_5)_2CH_2 + KNH_2 \tag{15}$$

are actually responsible for the effects observed. While we have no data concerning the occurrence of this reaction in liquid ammonia at −33°, the following experiments indicate that there is some ammonolysis at higher temperatures.

Expt. 1.—Potassium (0.3318 g.) was converted to KNH_2 in a two-legged liquid ammonia weighing tube[11] (20°, Fe catalyst) and allowed to react with 1.51 g. diphenylmethane (an excess). An orange-colored solution was formed. After two hours' reaction, solvent was evaporated, the tube was evacuated to a few tenths of a mm. at 90° and weighed. Loss in weight, 0.1384 g. or 96% of that calculated from equation (15) read from right to left. The ammonolysis of potassium diphenylmethyl under these conditions is therefore slight.

Expt. 2.—In a two-legged liquid ammonia reaction tube, 1.03 grams of diphenylmethane was allowed to react with the sodium amide from 0.34 g. sodium (2.4 moles). A deep-red solution was formed, which was concentrated to a few cc. over the excess amide and allowed to stand over night. A portion of the solution was then decanted into the clean leg of the reaction tube, the solvent was evaporated, and the substance was analyzed in the customary manner. The specimen tube was heated in a vacuum at 20°, and at 52°, there being no further loss at the latter temperature. The solid was a pale yellow, indicating extensive ammonolysis.

Found: Na, 11.5%. Calc'd for $(C_6H_5)_2CHNa$: Na, 12.1%.

Bromobenzene, sodium chloride and potassium amide.—To a solution of 0.0413 mole bromobenzene and 0.0232 mole sodium chloride in vessel *2* was added 0.0314 mole potassium amide (prepared in vessel *1*). After evaporation of the solvent, the chloride ion in the residue was found to correspond exactly with the sodium chloride used. The yield of bromide ion (57.8% theoretical) is the same as would be obtained without the addition of sodium chloride.

SUMMARY

(1) Potassium amide, or rather the amide ion, catalyzes the following reactions, which do not take place, or which proceed very slowly in the absence of a catalyst in liquid ammonia at −33°.

$$C_6H_5NHK + C_6H_5X = (C_6H_5)_2NH + KX$$
$$C_6H_5NHK + C_6H_5X = p\text{-}C_6H_5\cdot C_6H_4NH_2 + KX$$
$$(C_6H_5)_2NK + C_6H_5X = (C_6H_5)_3N + KX \; (X = Cl, Br, I)$$

The amide ion also accelerates the following reaction, which is otherwise very slow in ammonia at −33°.

$$(C_6H_5)_3CK + C_6H_5Cl \rightarrow KCl + (C_6H_5)_4C$$

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[11] Bergstrom, *J. Am. Chem. Soc.*, **53**, 4068–9 (1931).

Chlorobenzene and potassium phenolate do not react, either alone, or in the presence of potassium amide in ammonia at −33°.

(2) Diphenylmethylpotassium reacts slowly with chlorobenzene in the absence of potassium amide, and apparently catalyzes the reaction of potassium diphenylamide with chlorobenzene. The diphenylmethyl anion (a base in Brønsted's sense) is presumably the actual catalyst.

(3) The strongest bases (in the Brønsted sense) react most readily with the phenyl halides, and only the very strongest (NH_2^- and $(C_6H_5)_2CH^-$) catalyze reactions between the phenyl halides and salts of the type of potassium anilide, potassium diphenylamide, potassium quinaldyl, and potassium triphenylmethyl. The degree of dissociation of these salts seems to be of minor importance in their reactivity.