Relative Reactivities of Ammonia and Amide Ion in Addition to 4-Chlorobenzyne[1,2]

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Abstract: The relative reactivities of NH_2^- and NH_3 toward the two reactive positions of 4-chlorobenzyne are determined by the method of *ad eosdem* competition from the variation of *p-/m*-chloroaniline product ratio with KNH_2 concentration. Amide ion is estimated to be 2.4×10^2 times as reactive as ammonia toward the carbon meta to chlorine and 49 times as reactive toward the para carbon. The amide ion rates toward the two carbons are equal, but ammonia is 4.92 times as reactive toward the carbon para as toward that meta to chlorine. Previous data of similar type concerning rates of addition of methoxide ion and methanol toward 4-chlorobenzyne are recalculated by an improved method.

When direct measurement of reaction rates is not feasible, relative rates may often be determined by competition methods. In a familiar method,[3,4] two reagents compete for a reactive intermediate to give two different products. The relative rate constants for reactions with the two reagents are computed from yields of the two products, with attention to reagent concentrations.

The method of direct competition is not serviceable when a reactive intermediate gives with either of two reagents the same product. In the situation of immediate interest, the two reagents are a conjugate pair of nucleophiles, that is, a pair related as conjugate acid and conjugate base, as in the example of ammonia and amide ion. The consequence of the nucleophilic attack of either ammonia or amide ion on benzyne, in ammonia solution, is ultimately the formation of the same product, aniline.[5]

However, the relative reactivities of the members of a conjugate pair of nucleophiles can be determined from product yields if the reactive intermediate has two reactive sites, if the products from reaction at the two sites are distinguishable (as well as stable under the reaction conditions), and if the relative reactivities of the two nucleophiles with the two sites are different. The desired rate constant ratios are calculated from the variation of product ratio with reagent ratio. Inasmuch as *the same products* are formed by addition of either nucleophile, this is designated the method of *ad eosdem* competition.[6]

The method of *ad eosdem* competition was developed and employed by Bunnett and Pyun[7] to determine the relative reactivity of methanol and methoxide ion at the positions meta and para to chlorine in 4-chlorobenzyne. Simultaneously, the same principle was

developed by two other groups[8,9] for application to other systems.

Method of *ad eosdem* Competition. Let us consider the addition of ammonia to 4-chlorobenzyne, with and without catalysis by amide ion. The uncatalyzed addition is represented in Scheme I; for the catalyzed

Scheme I
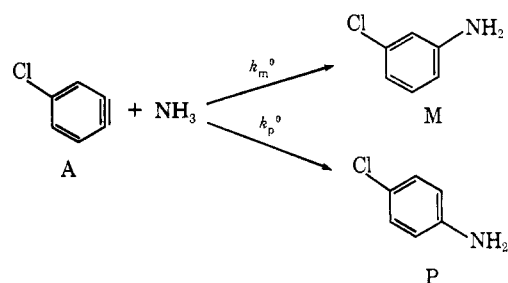
addition, the corresponding rate coefficients are symbolized k_m^- and k_p^-.

Assuming that uncatalyzed addition is first order in 4-chlorobenzyne (A) and in ammonia, that amide ion-catalyzed addition is first order in A and in amide ion and zero order in ammonia, and that variation of activity coefficients is negligible, we may write

$$d[P]/dt = k_p^0[A][NH_3] + k_p^-[A][NH_2^-] \quad (1)$$

$$d[M]/dt = k_m^0[A][NH_3] + k_m^-[A][NH_2^-] \quad (2)$$

where M and P are *m-* and *p*-chloroaniline.

Defining R as the experimental *p-/m*-chloroaniline ratio under any conditions, R^0 as k_p^0/k_m^0, the product ratio in reaction with neutral ammonia, and R^- as k_p^-/k_m^-, we may obtain from eq 1 and 2, after Bunnett and Pyun[7]

$$\frac{R^0 - R}{R - R^-} = \frac{k_m^-}{k_m^0} \frac{[NH_2^-]}{[NH_3]} \quad (3)$$

Further algebraic manipulation affords

$$\frac{R^0 - R}{R - R^-} = \frac{k_p^-}{k_p^0} \frac{R^0}{R^-} \frac{[NH_2^-]}{[NH_3]} \quad (4)$$

If R^0 and R^- can be determined, as well as R at several concentrations of amide ion, a plot of the quantity on

(1) Financial support by the National Science Foundation is gratefully acknowledged.

(2) Based on the Dissertation of J. K. Kim, June 1970; *Diss. Abstr. B*, **31**, 5879 (1971).

(3) G. A. Russell in "Investigation of Rates and Mechanisms of Reactions," 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, Chapter VIII.

(4) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 91.

(5) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).

(6) From the Latin *ad eosdem fructus*, to the same products.

(7) J. F. Bunnett and C. Pyun, *J. Org. Chem.*, **34**, 2035 (1969); *Amer. Chem. Soc., Div. Petroleum Chem., Prepr.*, **14**, C76 (1969).

(8) P. Haberfield and L. Seif, *J. Org. Chem.*, **34**, 1508 (1969).

(9) R. A. Sneen and H. M. Robbins, *J. Amer. Chem. Soc.*, **91**, 3100 (1969).

Table I. Reactions of p-Dichlorobenzene with KNH_2 in Ammonia[a]

Run	NH_3, ml[b]	K metal, mol × 10²	p-$C_6H_4Cl_2$, mol × 10³	Cl⁻, %[c]	$[KNH_2]_f$,[d] M	Chloroanilines Para, %	Chloroanilines Meta, %	R[e]
1[f]	500	0.90	0.20	104	0.012	57.0	12.4	4.60
2	500	1.22	0.22	105	0.017	57.6	12.8	4.50
3	500	2.96	0.20	116	0.049	52.7	13.1	4.02
4	250	2.60	0.20	109	0.085	49.3	13.7	3.60
5	250	4.11	0.20	107	0.140	52.7	16.9	3.12
6	250	5.35	0.20	108	0.183	52.0	18.7	2.78
7	250	6.66	0.22	115	0.228	52.1	19.2	2.71
8	100	3.31	0.20	110	0.276	52.3	20.6	2.54
9	100	4.22	0.20	106	0.359	50.4	22.0	2.29
10	100	5.11	0.20	106	0.438	48.8	23.8	2.05
11	100	6.64	0.20	108	0.574	48.5	25.0	1.94
12	50	5.26	0.20	114	0.899	45.2	27.4	1.65
13	50	7.74	0.22	115	1.34	43.5	30.2	1.44
14	50	10.86	0.20	115	1.89	40.9	30.3	1.35
15	50	15.37	0.22	114	2.69	37.4	30.4	1.23
16	50	20.95	0.20	116	3.68	36.7	31.6	1.16
17	50	30.20	0.22	118	5.13	35.1	31.9	1.10
18	50	69.80	0.29	122	g	30.6	29.1	1.05
19	50	74.88	0.31	120	g	30.5	29.1	1.05
20	200	5.30[h]	0.45	104	i	48.2	14.8	3.26
21	200	14.40[h]	0.46	108	i	45.7	15.2	3.01

[a] Reactions at reflux for 2.5 min, unless otherwise noted. [b] At ca. $-67°$. [c] On basis of one Cl⁻ per $C_6H_4Cl_2$ molecule. [d] $[KNH_2]$ at half reaction. [e] p-/m-Chloroaniline ratio. [f] Reaction time 10 min. [g] Saturated solution of KNH_2. [h] Na. [i] Saturated solution of $NaNH_2$.

the left side of eq 3 or 4 against $[NH_2^-]/[NH_3]$ should give a straight line whose slope is k_m^-/k_m^0 or $(k_p^-/k_p^0)(R^0/R^-)$.

Rearranging eq 3, we get

$$(R^0 - R)[NH_3]/[NH_2^-] = R(k_m^-/k_m^0) - R^-(k_m^-/k_m^0) \quad (5)$$

This implies that the desired rate constant ratios can be evaluated even if a direct experimental determination of R^- has not been made. The quantity on the left side of eq 5 is plotted against R, at each of several amide ion concentrations; the slope is k_m^-/k_m^0 and the intercept $-R^-(k_m^-/k_m^0)$. The negative of the intercept/slope ratio is then R^-, and k_p^-/k_p^0 is reckoned as $(k_m^-/k_m^0)(R^-/R^0)$.

Design of the Experiment. For the method of *ad eosdem* competition to be applicable for determination of the relative reactivities of amide ion and ammonia toward 4-chlorobenzyne, it must be demonstrated that m- and p-chloroaniline are stable to KNH_2 in ammonia. It was shown that either isomer gave only a trace (about 0.5%) of chloride ion on treatment with KNH_2 in ammonia under typical reaction conditions, and that neither underwent isomerization.

This condition being fulfilled, it was next necessary to choose a 4-chlorobenzyne precursor or precursors which would not give m- or p-chloroaniline by any alternative mechanism. p-Dichlorobenzene was the obvious candidate except for reactions in the absence of KNH_2.

Isomerization of p-dichlorobenzene on exposure to KNH_2 in ammonia is not expected. Strongly basic reagents do cause 1,2,4-tribromobenzene and 1,2,3,5-tetrachlorobenzene to isomerize and disproportionate,[10-12] but 1,2,4-trichlorobenzene does not take part in the base-catalyzed halogen dance. Inasmuch as oligohalobenzenes with fewer halogens are less prone

to participate in the halogen dance, oligochlorobenzenes are less reactive in this sense than are corresponding oligobromobenzenes, and 1,2,4-trichlorobenzene does not isomerize, isomerization of p-dichlorobenzene is not expected.

Conversion of p-dichlorobenzene directly to p-chloroaniline, by the S_NAr[13] or $S_{RN}1$[14] mechanism, is also not expected. Experiments with 5- and 6-halopseudocumenes[14] indicate that the chloro derivatives do not undergo direct aminodechlorination with KNH_2 in ammonia although such a process (via the $S_{RN}1$ mechanism) was observed for the iodo derivatives. Furthermore, if direct aminodechlorination played a substantial role, the proportion of p-chloroaniline among the products should increase with increase in KNH_2 concentration, but experimentally (vide infra) the opposite trend is observed.

For these reasons, p-dichlorobenzene was accepted as a satisfactory precursor of 4-chlorobenzyne for reactions with KNH_2 in ammonia.

However, p-dichlorobenzene does not react with neutral ammonia at $-33°$. 1-(4-Chloro-2-iodophenyl)-2-benzenesulfonhydrazide (1) was therefore chosen as the 4-chlorobenzyne precursor for the purpose of determining R^0. 1 reacts with alcoholic alkoxides to form 4-chlorobenzyne via 2-iodo-4-chlorophenyl anion (2);[15] cf. Scheme II. As described below, it was necessary to use a solution of an alkoxide base in ammonia to generate 4-chlorobenzyne from 1 at $-33°$.

Results

Reactions of p-Dichlorobenzene with KNH_2. Experiments were conducted at several KNH_2 concentrations, as listed in Table I. The p-/m-chloroaniline ratio (R) varied from 4.6 in very dilute (0.012 M) KNH_2 to 1.05

(10) J. F. Bunnett and C. E. Moyer, Jr., *J. Amer. Chem. Soc.*, **93**, 1183 (1971); J. F. Bunnett and G. Scorrano, *ibid.*, **93**, 1190 (1971).

(11) J. F. Bunnett, *Accounts Chem. Res.*, **5**, 139 (1972).

(12) M. H. Mach, unpublished observations.

(13) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); J. F. Bunnett, *Quart. Rev., Chem. Soc.*, **12**, 1 (1958).

(14) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463 (1970).

(15) J. F. Bunnett, D. A. R. Happer, M. Patsch, C. Pyun, and H. Takayama, *ibid.*, **88**, 5250 (1966).

Table II. Reactions of 1-(4-Chloro-2-iodophenyl)-2-benzenesulfonhydrazide (1) in Liquid Ammonia at Reflux

Added solute, M	[1], M	Reaction time, hr	I⁻	C₆H₅Cl	3	Chloroaniline Para	Meta	R
Nil	0.05	18[a]	32	1	18	15.1	4.0	3.79
CH₃ONa, 0.13	0.017	10[b]	22	5	14	3.52	0.712	4.94
(CH₃)₃COK, 0.13	0.012	1[c]	41	Trace	20	1.46	0.296	4.93
(CH₃)₃COK, 2.17	0.032	2.5[c]	61	2	23	1.87	0.381	4.91

[a] Reaction in sealed tube at 58°. [b] Small amount of chloroanisoles detected as products by glpc. [c] Large amounts of unidentified products detected by glpc.
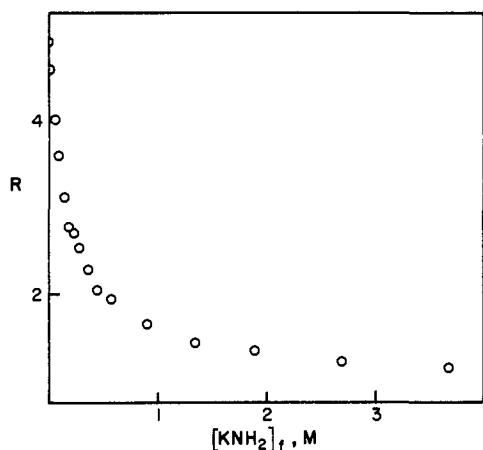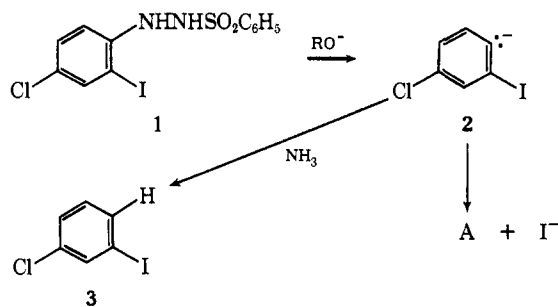

Figure 1. Variation in p-/m-chloroaniline product ratio (R) with KNH₂ concentration; data from Table I except that for [KNH₂]ₜ = 0, which is from Table II.

Scheme II

in saturated (ca. 6.1 M)[16] KNH₂ solutions.[17] The variation in this ratio up to 3.68 M KNH₂ is displayed in Figure 1. (The KNH₂ concentration listed in Table I, symbolized [KNH₂]ₜ, is that which prevailed at half completion of reaction.)

The yield of chloride ion was measured in all experiments. It somewhat exceeded one chloride ion per molecule of p-dichlorobenzene, ranging from 104 to 122% of expectation on that basis. The higher yields of chloride ion were observed for the most part at higher KNH₂ concentrations.

The sum of the p- and m-chloroaniline yields was about 70% in most experiments, but it was closer to 60% in three runs. No p-dichlorobenzene was recoverable from any run. Inasmuch as the formation of a chloroaniline from p-dichlorobenzene involves

the loss of only one chlorine atom per molecule of the latter, the total chloroaniline yield must fall short of 100% at least to the extent that the chloride ion yield exceeds 100%. However, the shortfall is greater than that in all cases, and much greater in some.

The last two runs of Table I involve NaNH₂ instead of KNH₂. The solubility of NaNH₂ in ammonia is quite low, and both experiments involve saturated solutions, the concentration of which at −33° is ca. 0.017 M.[16] The observed p-/m-chloroaniline ratios for these runs are about the same as for 0.14 M KNH₂.

Reactions of 1-(4-Chloro-2-iodophenyl)-2-benzenesulfonhydrazide (1). It was originally hoped that liquid ammonia would be sufficiently reactive at −33° to bring about decomposition of 1 according to Scheme II. However, no chemical change was detectable at that temperature. On the other hand, reaction did occur in a sealed tube at 58°, as reported in Table II, but the p-/m-chloroaniline ratio observed (3.79) was not a reasonable extrapolation from the ratios at low KNH₂ concentrations in Table I. Plausibly, the discrepancy could be attributed to the difference in temperature.

Metal alkoxides were therefore employed to generate 4-chlorobenzyne from 1 at −33°. Sodium methoxide is known[15] to effect decomposition of 1 in methanol at 59°, and we found that it also causes decomposition in ammonia at −33°. Decomposition was also brought about by potassium $tert$-butoxide at −33°. These experiments are detailed in Table II. The yields of chloroanilines obtained were rather low, but the p-/m-chloroaniline ratios (ca. 4.92) were in harmony with ratios at low KNH₂ concentrations in Table I.

All the runs of Table II produced substantial amounts of m-chloroiodobenzene (3), which is to be anticipated if proton capture by anion 2 competes effectively with iodide ion loss;[18] cf. Scheme II. The small amounts of chlorobenzene obtained are probably the consequence of electron transfer by some suitable electron donor to m-chloroiodobenzene, and then iodide ion loss from the radical anion thus formed;[19] that side reaction should have no effect on the relative yields of p- and m-chloroaniline.

Discussion

The data of Table I show that, in reactions of p-dichlorobenzene with KNH₂ in liquid ammonia, there is a substantial variation of the p-/m-chloroaniline product ratio (R) with KNH₂ concentration. The variation is plotted in Figure 1. In order to treat these data according to eq 3 or 4, one must utilize values for

(16) P. W. Schenk and H. Tulhoff, *Ber. Bunsenges. Phys. Chem.*, 71, 210 (1967); *cf.* also E. C. Franklin, *Z. Phys. Chem.*, 69, 290 (1909).

(17) E. R. Biehl, E. Nieh, H.-M. Li, and C.-I. Hong, *J. Org. Chem.*, 34, 500 (1969), have observed that orientation of ammonia addition to benzyne carboxylates (from halobenzoic acids) is different with NaNH₂ in ammonia than with KNH₂ in ammonia. The differences were attributed to differences in amide ion concentration between the two systems.

(18) *Cf.* J. A. Zoltewicz and J. F. Bunnett, *J. Amer. Chem. Soc.*, 87, 2640 (1965); J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, 31, 2369 (1966).

(19) *Cf.* J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, 89, 6712 (1967); and ref 14.

R^0 and R^-, the product ratios for uncatalyzed addition of ammonia and for amide ion-catalyzed addition, respectively. For R^0, the observed R value from the methoxide- or *tert*-butoxide-induced decomposition of **1** in ammonia at $-33°$ (Table II), namely 4.92, was chosen, and 4.92 is also a reasonable extrapolation of the R values at low KNH_2 concentrations in Figure 1. For R^-, we first tried the experimental R value from experiments at high (saturated) KNH_2 concentrations, which is 1.05 (Table I).

The plot of $(R^0 - R)/(R - R^-)$ *vs.* $[KNH_2]_f/[NH_3]$ thus obtained is not displayed; it was linear for KNH_2 concentrations through 1.89 M, but curved upward at higher concentrations. The nature of the function plotted is such that any experimental error in determination of R or any systematic error owing, for example, to an imperfect choice of R^- would have a huge effect on the magnitude of $(R^0 - R)/(R - R^-)$ at higher KNH_2 concentrations where the denominator is a small difference between large quantities. As explained below, the reason for the upward curvature is that 1.05 is somewhat higher than the true value of R^-.

Because of the sensitivity of $(R^0 - R)/(R - R^-)$ to the magnitude of the denominator, the experimental points were weighted[20] according to $(R - R^-)$ for purposes of linear regression analysis. For all points up to and including 1.89 M KNH_2, the resulting slope was 242 $\pm$ 4 and the intercept 0.01 $\pm$ 0.04. The intercept is not significantly different from zero, in accordance with eq 3 or 4. The slope provides an evaluation of k_m^-/k_m^0 as 242 $\pm$ 4.

A plot of $(R^0 - R)[NH_3]/[KNH_2]_f$ against R (*cf.* eq 5), utilizing all data in Table I through 5.13 M KNH_2, is presented as Figure 2. The plot is linear as expected except for the deviation of the two points at the far right which represent the two lowest concentrations of KNH_2. Deviation of those two points is not surprising inasmuch as the function plotted vertically is sensitive to small errors in $[KNH_2]_f$ when that quantity is very small. Small losses of KNH_2 owing to neutralization by adventitious traces of acidic impurities, especially water and CO_2, would cause deviation in the sense observed. Therefore, in linear regression analysis of the plot in Figure 2, points were weighted according to $[KNH_2]_f$. The resulting linear regression line is drawn in Figure 2; it has slope 239 $\pm$ 6 and intercept -243 $\pm$ 9. With reference to eq 5, k_m^-/k_m^0 is thereby evaluated as 239 $\pm$ 6 and R^- as 1.02 $\pm$ 0.06.

With the use of 1.02 for R^-, all the data through 5.13 M KNH_2 were again treated according to eq 3, and a better correlation was obtained than when 1.05 had been employed for R^-. However, an even better correlation was obtained when 1.00 was used for R^-; the slope was 232 $\pm$ 5 and the intercept -0.02 $\pm$ 0.08.

Since 1.00 is within experimental error of the negative of the intercept/slope ratio from Figure 2 and gives a superior correlation according to eq 3, it is chosen as the best value for R^- or k_p^-/k_m^-. k_m^-/k_m^0 is then 2.4 $\times$ 10^2, and k_p^-/k_p^0 is 49. If k_m^0 is arbitrarily assigned the value 1.00, k_p^0 is 4.92 and k_m^- and k_p^- are both 240.

Using these relative rate values, one reckons that in a saturated solution of KNH_2 in ammonia, which is about 6.1 M according to the data of Schenk and
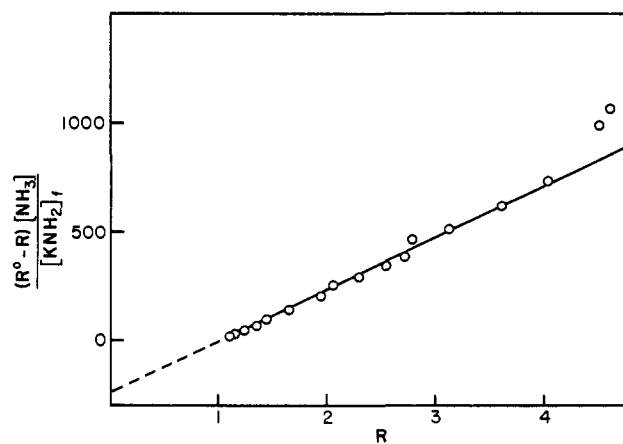

Figure 2. Plot of data according to eq 5.

Tulhoff,[16] the p-/m-chloroaniline product ratio should be 1.08. Runs 18 and 19 in Table I involve saturated solutions, and in both of them the observed R was 1.05. The observed R of 1.10 in run 17 is exactly as called for by the chosen relative rate values.

Side Reactions. We now inquire why the chloride ion yields in Table I exceed 100% and why the sum of m- and p-chloroaniline yields is at most 74%. Also, why does the sum of chloroaniline yields fall short of 100% by more than the chloride ion yield exceeds 100%? Could the side reactions thus indicated have affected the p-/m-chloroaniline ratios observed?

Reaction of the chloroaniline products, or rather the chloroanilide ions, with KNH_2 is clearly not the source of the excess chloride ion. The chloroanilines release only about 0.5% of chloride ion on exposure to KNH_2 in ammonia under the conditions of our determinations. The chloroanilide ions are inert because the negative charge is extensively delocalized to ring carbon atoms where it protects the ring hydrogens from attack by amide ion,[21] and thus blocks the first step toward formation of an aryne.[5]

To the extent that the 4-chlorobenzyne originally produced underwent further reaction with KNH_2 to form 1,3- or 1,4-benzdiyne, more than one chloride ion would be generated per molecule of p-dichlorobenzene. The fact that the yield of chloride ion generally increases with an increase in KNH_2 concentration is in accord with this extraordinary hypothesis, but there is no compelling evidence for it.

Inasmuch as the reaction of chlorobenzene with KNH_2 in ammonia forms di- and triphenylamine as well as aniline,[22] we sought bis(chlorophenyl)amines among the products from p-dichlorobenzene but found none. The possibility that bis(chlorophenyl)amines would not survive exposure to KNH_2 is countered by the fact that even N-phenyl-3-iodoaniline releases only 15% of iodide ion on 11 min exposure to 0.16 M KNH_2 in ammonia at reflux;[2] this compares with 5% release from m-iodoaniline and 0.5% release of chloride ion from m-chloroaniline under the same conditions. A tris(chlorophenyl)amine would be expected to react rapidly with KNH_2 to release all three chlorines as chloride ion, but such a complication therefore cannot ac-

(20) J. Topping, "Errors of Observation and Their Treatment," 3rd ed, Chapman and Hall, London, 1962, p 109.

(21) J. F. Bunnett and B. F. Hrutfiord, *J. Amer. Chem. Soc.*, **83,** 1691 (1961).

(22) F. W. Bergstrom, R. E. Wright, C. Chandler, and W. A. Gilkey, *J. Org. Chem.*, **1,** 170 (1936).

count for the discrepancy between the deficiency in chloroaniline yields and the surplus of chloride ion. If any tris(aminophenyl)amines were formed, they would probably have escaped detection by the procedures we employed.

If bis- or tris(chlorophenyl)amines were formed, their formation would not affect the p-/m-chloroaniline ratio insofar as consumption of 4-chlorobenzyne is concerned, but this ratio would be affected if one of the chloroanilide ions (meta or para) were more reactive than the other in adding to 4-chlorobenzyne. We have no evidence on this question, but we doubt that there would be a great enough difference in reactivity seriously to affect the observable p-/m-chloroaniline ratios.

Interpretation of Relative Reactivities. The equality or virtual equality of rates of addition of amide ion to the two aryne positions of 4-chlorobenzyne might suggest that both rates are encounter-controlled. If so, absolute values for rate coefficients could be estimated. However, it is unlikely that those rates are encounter-controlled because there is strong orientation in the addition of amide ion to 3-halobenzynes. The m-/o-haloaniline ratio from addition to 3-fluorobenzyne[23] or 3-chlorobenzyne[2] is about 100. If the rate of addition were encounter-controlled, the m-/o-haloaniline ratio should be nearly unity, being exalted only by a slight steric deceleration of addition ortho to halogen.

As discussed elsewhere,[15] the fact that the p-/m-chloroanisole ratio from methoxide ion-catalyzed addition of methanol to 4-chlorobenzyne is less than for uncatalyzed addition is evidence for a stepwise mechanism of addition, and against a mechanism of concerted, four-center addition which had been proposed earlier. Concerted addition is also contraindicated by orbital symmetry considerations.[24] Nevertheless, the concerted mechanism was advocated in an otherwise authoritative recent review.[25]

The present observation of a strong substituent effect on the uncatalyzed addition of ammonia but the absence of substituent effect on the amide ion-catalyzed addition also calls for a stepwise mechanism of addition, by the same reasoning. The lack of substituent effect in the amide ion-catalyzed addition indicates that there is very little C–N bond formation at the transition states (e.g., **4**) for attachment of amide ion to aryne
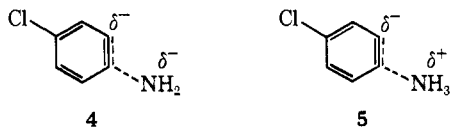
carbon. On the other hand, there is considerable C–N bond formation at the transition states (e.g., **5**) for attachment of the weaker nucleophile ammonia, and therefore more development of negative charge on carbon and a substantial orientation effect.

Methoxide Ion/Methanol Reactivity Ratio toward 4-Chlorobenzyne. Bunnett and Pyun[7] showed that the p-/m-chloroanisole ratio in addition of methanol to 4-chlorobenzyne varied from 4.73 in the absence of

(23) G. B. R. de Graaff, H. J. den Hertog, and W. C. Melger, *Tetrahedron Lett.*, 963 (1965).

(24) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971); R. G. Pearson, *ibid.*, **4**, 152 (1971).

(25) R. W. Hoffmann in "Chemistry of the Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 1096.

methoxide ion to 2.12 in 1.9 M NaOCH$_3$. The variation at intermediate methoxide concentrations was similar to that in Figure 1. They chose 4.73 as R^0 and 2.12 as R^- and treated their data according to the analog of eq 3, but they did not give or utilize an equation such as eq 5.

A plot of $(R^0 - R)/[\text{NaOCH}_3]_t$ against R, based on their data, is a good approximation to a straight line. The plot is not shown. Linear regression analysis was performed with points weighted by $[\text{NaOCH}_3]_t$. The slope is 4.91 ± 0.32 and the intercept -9.36 ± 0.82. From these values and the concentration of methanol solvent (23.6 M), one reckons k_m^-/k_m^0 as 116 ± 8, k_p^-/k_p^0 as 47 ± 4, and R^- as 1.91 ± 0.30. If k_m^0 is assigned the value 1.00, k_p^0 is then 4.7, k_m^- is 1.2×10^2, and k_p^- is 2.2×10^2. From these values, the observable R in 1.90 M NaOCH$_3$ should be 2.18, which compares with 2.12 as reported by Bunnett and Pyun.

We conclude that these relative rate values resulting from recomputation of their data by an analog of eq 5 are more accurate than the relative rates reckoned previously.[7] The correction is not large, however.

Summary

The relative rate constants for addition to 4-chlorobenzyne in the amide ion–ammonia and methoxide ion–methanol systems are summarized in Table III.

Table III. Summary of Relative Rate Constants for Addition of Nucleophiles to 4-Chlorobenzyne

Rate constants	KNH$_2$–NH$_3$ system ($-34°$)[a]	NaOCH$_3$–CH$_3$OH system ($59.6°$)[b]
k_m^0	(1.00)	(1.00)
k_p^0	4.92	4.73
k_m^-	2.4×10^2	1.2×10^2
k_p^-	2.4×10^2	2.2×10^2
k_p^-/k_m^-	1.00	1.91
k_p^-/k_p^0	49	47

[a] This work. [b] From data of Bunnett and Pyun,[7] as recalculated in this work.

Any comparison of the relative reactivities in methanol addition with those in ammonia addition must take account of the considerable difference in temperature of reaction in the two studies; the methanol studies were conducted at 59° and the ammonia studies at $-34°$. The difference in the R^0 value between the first run and the other runs in Table II shows that the temperature factor is substantial.

Experimental Section

Materials. p-Dichlorobenzene was a commercial preparation of good quality. 1-(4-Chloro-2-iodophenyl)-2-benzenesulfonhydrazide (**1**) was prepared as previously described; the product thrice recrystallized from ethanol had mp 174–175° dec.

Reactions of p-Dichlorobenzene with KNH$_2$. All operations were conducted in three-neck, round-bottom flasks equipped with condensers chilled by solid CO$_2$ in 2-propanol with access to the atmosphere only through soda lime drying tubes. Ammonia from a commercial cylinder was condensed in such a flask immersed in a slush of solid CO$_2$ in 2-propanol, and small pieces of potassium metal were added (to destroy traces of water) until a blue color persisted. The ammonia was then distilled into an ammonia storage flask of similar type. The latter flask was equipped with a 50-ml pipet of special design.

The pipet was firmly mounted in a neck of the storage flask by means of a male standard taper joint, with the pipet tip immersed deeply into that flask. The upper part of the pipet was surrounded

by a slush of solid CO_2 in 2-propanol, and just beneath the lower measuring mark was a three-way stopcock which allowed ammonia to be drawn into the pipet from the storage flask and then released through another tube into a reaction flask. In this way, transfers from the storage flask to the reaction flask could be made accurately without loss by volatilization and without exposure to the external atmosphere. The temperature in the storage flask was measured as -65 to $-68°$.

Potassium metal was weighed *in vacuo*. The crusts from a small bar of potassium metal were cut away with a knife and the shiny lump was washed with dry pentane. The lump was quickly placed in a 10-ml flask filled with pentane and the glass stopper for the flask, in which was sealed a stopcock, was quickly put in place. A vacuum was applied through the stopcock, causing the pentane to evaporate. After evacuation, the stopcock was closed, the flask was weighed, and the weight of the empty flask and stopper was subtracted. Liquid anhydrous diethyl ether was then admitted through the stopcock.

After the desired volume of ammonia had been placed in the reaction flask, the weighed lump of potassium was quickly dropped in through the condenser and a minute amount of ferric nitrate nonahydrate was added to catalyze formation of KNH_2. The solution was stirred by a magnetic stirrer. After the blue color had disappeared (usually 10 min or longer), a weighed amount of *p*-dichlorobenzene dissolved in diethyl ether (1.0 ml per 50 ml of ammonia) was injected by means of a syringe through a rubber septum covering one neck of the reaction flask.

The reaction was strongly exothermic, causing vigorous ebullition of the ammonia, and caution was needed during addition of the dichlorobenzene. The reaction time, from addition of the dichlorobenzene to quenching by addition of powdered ammonium nitrate, was measured with a stopwatch. A measured amount of internal standard for glpc purposes (*o*-bromoaniline in hexane solution) was then added and the ammonia was allowed to evaporate overnight through a soda lime tube. To the residue was added water, the layers were separated, the hexane layer was analyzed by glpc, and the water layer was titrated for chloride ion with $AgNO_3$ after acidification with HNO_3. The glpc instrument was a Varian Aerograph Model 200 equipped with flame ionization detector and Disc integrator, and the column used was 5% Amine 220 on Chromosorb W (nonacid washed), 3.2 mm in diameter and 9.15 m long, operated at 145° with flow rate 38 ml/min. Glpc area readings were corrected for differential molar responses, determined together with retention times on mixtures of known composition.

Tests were made, involving trapping in dilute HCl solutions and back-titration with NaOH, to determine the amount of ammonia lost through the condenser during typical reactions of KNH_2 with *p*-dichlorobenzene. Also determined was the amount of ammonia held up as liquid wetting the walls of the condenser. Loss through the condenser was negligible, less than 0.1 ml of liquid ammonia. Hold-up in the condenser was about 1.7 ml of liquid ammonia.

Reactions of 1-(4-Chloro-2-iodophenyl)-2-benzenesulfonhydrazide (1). For reactions at $-34°$, the equipment used was the same as described above. Weighed amounts of **1** and metal alkoxide ($NaOCH_3$ or $KOC(CH_3)_3$) were placed in the reaction flask, and liquid ammonia was added thereto. Upon addition of the ammonia, the reaction mixture began to develop color, ultimately a deep orange-brown. The reaction was quenched by addition of powdered NH_4NO_3 after times listed in Table II. Product analysis was conducted much as described above. For glpc, *o*-chloroiodobenzene and/or *m*-dibromobenzene were employed as internal standards, and a column of 2% Amine 220 on Chromosorb G (nonacid washed), 3.2 mm in diameter and 9.75 m long, operated at 146° with flow rate 30 ml/min, was used.

For the reaction at 58°, a weighed amount of powdered **1** was placed in a heavy-walled Pyrex tube, the tube was cooled by liquid nitrogen, and liquid ammonia was added to it by means of a cooled pipet. After the ammonia had solidified, the tube was sealed, placed within an iron pipe, and heated in a water bath at 58° for 18 hr. The tube was again cooled in liquid nitrogen before it was opened. Product analysis was as described above.

Calculations. From the volume of ammonia measured (at *ca.* $-67°$) and the weight of potassium metal used, were calculated (a) the weight of ammonia used, with reference to density data,[26] (b) the weight of NH_3 consumed by reaction with K and the weight of KNH_2 formed, (c) the volume occupied by the resulting solution at $-33.5°$, with reference to density data,[16] (d) the moles of KNH_2 present after reaction with *p*-dichlorobenzene was half complete, by subtracting from the original moles of KNH_2 the moles of chloride ion formed in the reaction (the reaction ultimately consumes 2 equiv of KNH_2, one to form a chloroaniline, the other to convert it to chloroanilide ion), and (e) the KNH_2 and NH_3 molar concentrations present at half-reaction. These molar concentrations were employed in treatment of data according to eq 3 or 5. Linear regression analysis was performed on an Olivetti Programma 101 programable calculator. The uncertainties reported for the resulting rate ratios are standard deviations.

(26) J. Jander, "Anorganische und Allgemeine Chemie in Flüssigem Ammoniak," Interscience, New York, N. Y., 1966, p 16.