Tetrahedron, 1966, Vol. 22, pp. 1527 to 1537. Pergamon Press Ltd. Printed in Northern Ireland

1,5-HYDROGEN TRANSFER DURING DIAZONIUM ION DECOMPOSITION—IV

THE COPPER CATALYZED REACTION. A CASE OF HYDROGEN ATOM OR HYDRIDE ION TRANSFER IN THE SAME SYSTEM[1,2]

A. H. Lewin, A. H. Dinwoodie and T. Cohen
Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania 15213

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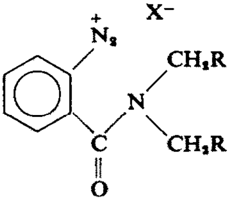
Abstract—Diazonium salts derived from *o*-amino-N,N-dialkylbenzamides have been found to undergo two discrete modes of decomposition. The thermal reaction involves a phenyl cation and yields (1) nucleophilic substitution products, (2) ring-closure products and (3) N-alkylbenzamides, which are produced along with aldehydes and ketones in a reaction involving a 1,5-hydride ion transfer. In contrast, no ring-closed products are formed in the copper catalyzed reaction. This reaction involves an intermediate phenyl radical which can (1) accept a ligand radical from a cupric salt to yield a substitution product or (2) undergo a 1,5-hydrogen atom transfer leading to a new radical which, after oxidation by cupric ion, yields the N-alkylbenzamide and the aldehyde or ketone. Either radical can abstract a hydrogen atom from an appropriate donor. This appears to be the first case in which it is possible to observe either a hydride ion or a hydrogen atom transfer in the same system. Experimental results which throw some light on the role of cuprous ions in the "copper catalyzed" diazonium ion decompositions are discussed. In this connection, cuprous oxide has been found to be extremely effective in promoting the radical decomposition of diazonium salts.

INTRODUCTION

Decomposition reactions of aromatic diazonium salts have been widely utilized for replacing substituents on the aromatic nucleus, for coupling and for ring closure.[3] Such reactions have been promoted by heat, copper powder, cuprous salts or light, and frequently by a combination of some of these.

In our investigation of the reactions of diazonium salts (I) derived from *o*-amino-N,N,-disubstituted benzamides, we have found two discrete modes of decomposition, involving intramolecular hydrogen atom and hydride ion transfer for the copper catalyzed and thermal reactions, respectively.



$R = H$ or C_6H_5

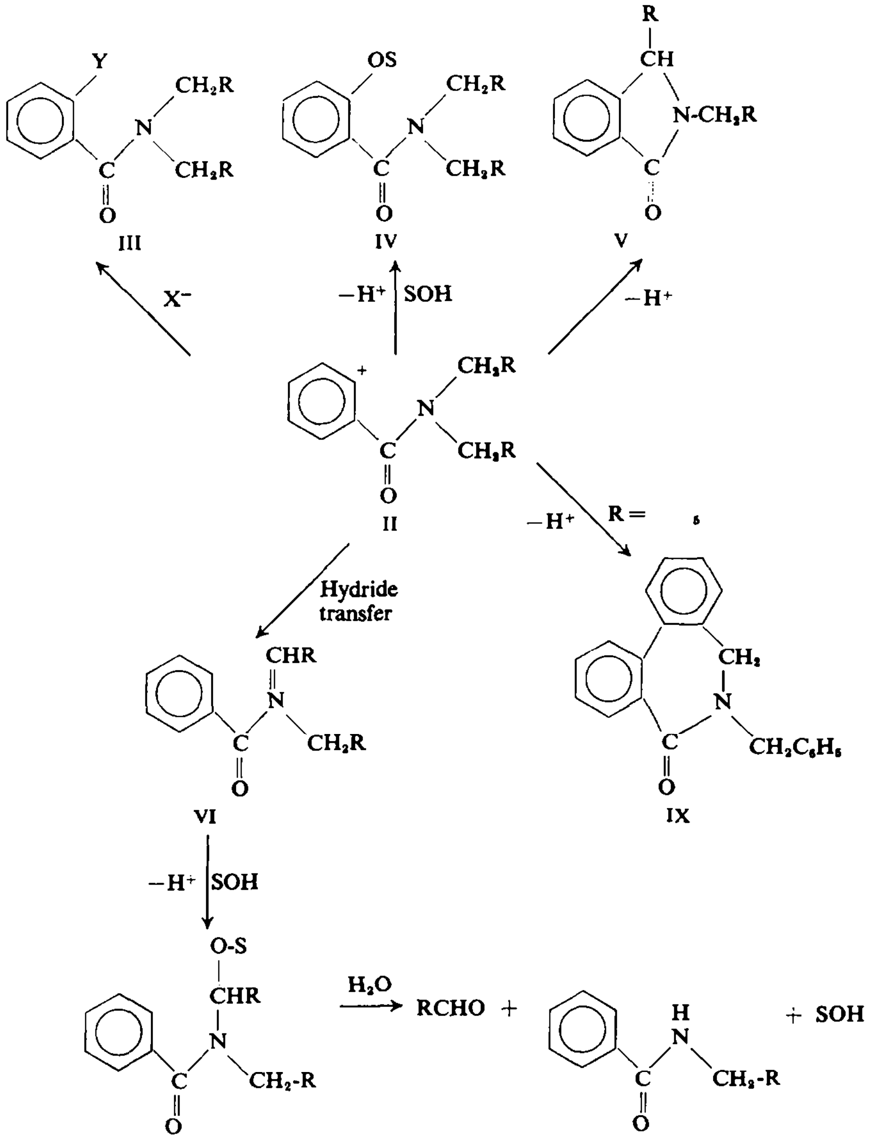
I

[1a] This investigation was supported by Grant GP 3821 from the National Science Foundation; [b] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept. 1965, Abstracts p. 54S.

[2] Part III: J. Lipowitz and T. Cohen, *J. Org. Chem.* **30**, 3891 (1965).

[3] For an authoritative review of diazonium ion chemistry, see: H. Zollinger, *Diazo and Azo Chemistry*. Interscience, New York (1961).

SCHEME A



The products obtained upon thermal decomposition of I and the probable paths for their formation are shown in Scheme A.[4] The earlier work has provided evidence that the reaction is heterolytic in character. The phenyl cation (II)[5] generated by loss

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[4a] T. Cohen, R. M. Moran, Jr. and G. Sowinski, *J. Org. Chem.* **26**, 1 (1961); [b] T. Cohen, A. H. Dinwoodie and L. D. McKeever, *Ibid.* **27**, 3385 (1962); [c] T. Cohen and J. Lipowitz, *J. Amer. Chem. Soc.* **86**, 2514 (1964); [d] T. Cohen and J. Lipowitz, *Ibid.* **86**, 2515 (1964).

[5] The structure II is not meant to preclude a triplet electronic state[6] or association of the cation with a molecule of N_2.[7]

[6] R. W. Taft, *J. Amer. Chem. Soc.* **83**, 3350 (1961).

[7] E. S. Lewis and J. M. Insole, *J. Amer. Chem. Soc.* **86**, 34 (1964).

of nitrogen from the diazonium ion, could give (a) substitution products (III, e.g., Y = F when X = BF_4)[8] and IV, which result respectively from reaction with the counterion X^- and with the solvent,[9] (b) the phthalimidine (V) formed by direct attack of the positive carbon atom of II on the N-alkyl group,[4d] and (c) the N-alkylbenzamide (VIII) which results, along with an aldehyde, from an intramolecular hydride ion transfer. In the N,N,-dibenzyl case (I; R = C_6H_5), the phenyl cation (II; R = C_6H_5) can also execute an intramolecular electrophilic substitution to produce 6-benzyl-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine-7-one (IX). The intermediate (VI; R = C_6H_5) which is involved in path (c), has been detected spectroscopically and independently prepared.[4c] A study of solvent effects using the related N,N-dicyclohexyl system has revealed that the importance of the various reaction paths available to the ion II is strongly influenced by the state of ion-association of the diazonium salt.[8]

RESULTS AND DISCUSSION

The product composition from the copper metal catalyzed decomposition of the diazonium hydrogen sulfate salt (I; R = C_6H_5, X = HSO_4) derived from *o*-amino-N,N-dibenzylbenzamide in acetic–sulfuric acid is markedly different from that reported[4b] previously for the thermal decomposition in the same medium (Table 1).

TABLE 1. DECOMPOSITION PRODUCTS OF N,N-DIBENZYLBENZAMIDE-*o*-DIAZONIUM HYDROGEN SULFATE IN 2N SULFURIC ACID IN ACETIC ACID

			Product Yields (%)[a,b]					
Temp	Cat.	Additive	Phthalimidine V; R = C_6H_5	Azepinone IX	N-benzylbenzamide[c] VIII; R = C_6H_5	Phenol IV; S = H R = C_6H_5	t-Amide XII R = C_6H_5	Total recovery
45°	—	—	3	12	33	52	nil	85
23°	Cu[d]	—	nil	nil	61	39	nil	88
23°	Cu[d]	C_6H_5SH[e]	nil	nil	74	18	8	97

[a] As isolated by alumina chromatography. [b] Normalized to 100%. [c] Benzaldehyde was produced in comparable yield. [d] 0·25 g atom/mole of amine. [e] 0·4 mole/mole of amine.

The ring closed products (V; R = C_6H_5 and IX) are not formed in detectable quantities in the copper catalyzed reaction. This suggests that the phenyl cation (II) which is thought to be the precursor of both ring-closed products in the thermal reaction, is not an intermediate in the catalyzed reaction. Furthermore, the ratio of hydrogen transfer product (VIII; R = C_6H_5) to N,N-dibenzylsalicylamide (IV; R = C_6H_5, S = H, formed in work-up by hydrolysis of the corresponding acetate and/or hydrogen sulfate ester) is about twice as great in the catalyzed as in the thermal reaction. These changes in product composition can not be due to the 22° temperature difference between the catalyzed and the thermal reactions since the product composition of the latter is quite insensitive to temperature changes.[4b] Whereas the addition of thiophenol does not change the product composition in the thermal

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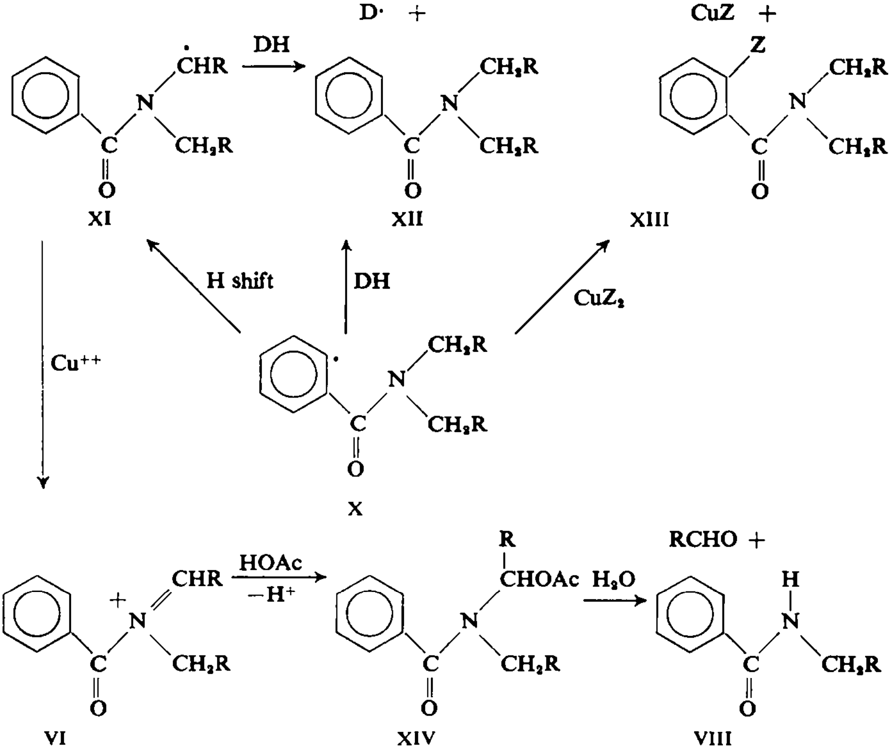
[8] T. Cohen and J. Lipowitz, *Tetrahedron Letters* 3721 (1964).

[9] This type of carbonium ion is capable of abstracting a chloride ion from some chlorinated solvents[8] as well as of forming typical solvolytic products.

reaction,[4b] its addition, in the copper catalyzed reaction, leads to the production of N,N,-dibenzylbenzamide, presumably by hydrogen atom abstraction from the additive by an intermediate radical. Indeed, all of these observations are consistent with a change from an ionic to a radical mechanism in proceeding from the thermal to the copper catalyzed reaction. It has been suggested several times in the literature[10,11] that copper catalyzed diazonium ion reactions are radical in character, although experimental evidence on this point is rather sparse.

The products of the copper catalyzed reaction can be reasonably explained by the sequence in Scheme B, which is based on the mechanisms of the Sandmeyer[12,13] and Meerwein[12–14] reactions. Reduction of the diazonium ion by copper metal or by cuprous ion, which is presumably present on the surface of the metal, produces nitrogen and the phenyl radical (X; R = C_6H_5). The latter can suffer a 1,5-hydrogen

SCHEME B



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[10] W. A. Waters, *The Chemistry of Free Radicals* p. 165. Clarendon Press, Oxford (1946); D. H. Hey and T. M. Moynehan, *J. Chem. Soc.* 1563 (1959); G. H. Williams, *Homolytic Aromatic Substitution* p. 28. Pergamon Press, New York (1960); L. G. Markova and M. K. Matveeva, *Izvest. Akad. Nauk. SSSR, Otdel. Khim. Nauk*, 1974 (1960); R. Huisgen and W. D. Zahler, *Chem. Ber.* **96**, 736 (1963); R. A. Abramovitch and G. Tertzakian, *Canad. J. Chem.* **43**, 940 (1965).

[11] D. F. De Tar, *Organic Reactions* Vol. 9; Chap. 7. Wiley, New York (1957).

[12] J. K. Kochi, *J. Amer. Chem. Soc.* **79**, 2942 (1957).

[13] D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc.* **A242**, 16 (1957).

[14] S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Org. Chem.* **21**, 380 (1956); C. S. Rondestvedt, Jr., *Org. Reactions* Vol. 11; Chap. 3. Wiley, New York (1960).

atom transfer[15] to produce the more stable radical (XI; R = C_6H_5), abstract a hydrogen atom from an external donor (DH) to produce N,N-dibenzylbenzamide (XII; R = C_6H_5) or it can accept a ligand radical from a copper (II)[16] salt (ligand radical transfer),[17–21] to produce substitution products (XIII). The new radical (XI) can possibly abstract a hydrogen atom from an external donor to yield N,N-dibenzylbenzamide (XII; R = C_6H_5) or it can be oxidized by copper (II) to the cation (VI) which is also an intermediate in the ionic reaction. In acetic acid, this intermediate would be expected to form the α-acetoxyamide (XIV; R = C_6H_5) which would hydrolyze in work-up to benzaldehyde and N-benzylbenzamide.[22] (*vide infra*)

Evidence concerning this scheme has been sought by comparing product compositions in the thermal and copper catalyzed reactions of the diazonium fluoroborate (I; R = H, X = BF_4) derived from *o*-amino-N,N-dimethylbenzamide.[4a] Unlike the dibenzyl analogue, this salt is soluble in water, as well as in acetic acid. Ligand radical transfer of H_2O^+ is expected to be considerably slower than that of the acetoxy group.[18] Furthermore, the products in the dimethyl case are much more amenable to accurate VPC analysis than are those from the dibenzylamide.

The products of thermal decomposition of I (R = H, X = BF_4) are similar to those previously obtained by decomposition of the corresponding hydrogen sulfate salt in aqueous sulfuric acid.[4a] The yields in the thermal and copper catalyzed reactions are compared in Table 2. The product composition is again seen to be quite temperature insensitive in the thermal reaction, both in water and in acetic acid;[23] it is, however, markedly changed by copper catalysis of the reaction. The change is clearly of the type expected if the phenyl cation (II; R = H) is regarded as an intermediate in the thermal but not in the copper catalyzed reaction. The compounds (V; R = H and III; Y = F) which can only be formed from this carbonium ion are not among the products of the copper catalyzed reaction. The nearly exclusive formation of hydrogen transfer product, N-methylbenzamide (VIII; R = H), in water, is completely consistent with the mechanism proposed in Scheme B, since neither a good

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[15] D. N. Brown, D. H. Hey and C. W. Rees, *J. Chem. Soc.* 3873 (1961).

[16] The copper (II) could be generated by disproportionation of copper (I) ions or by oxidation of copper (I) by the diazonium salt.

[17] J. K. Kochi, *Tetrahedron* **18**, 483 (1962); J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.* **87**, 1508 (1965); J. K. Kochi and D. M. Mog, *Ibid.* **87**, 522 (1965).

[18] H. Taube and H. Meyers, *J. Amer. Chem. Soc.* **76**, 2103 (1954); H. Taube, *Advances in Inorganic Chemistry and Radiochemistry* (Edited by H. J. Emeleus and A. G. Sharpe) Vol. 1; pp. 1–50. Academic Press, New York (1959).

[19] We prefer the term "ligand radical transfer" as being more descriptive than the previously suggested terms, ligand transfer,[17] and redox transfer.[20] It should be noted that the net result of this process is the transfer of a radical rather than an anion.

[20] H. Asscher and D. Vofsi, *J. Chem. Soc.* 3921 (1963).

[21] The alternative electron transfer process[17,18] can be ruled out on the basis of the absence of ring closed products. This is expected since this process would result in the very unstable phenyl cation.[17]

[22] A direct ligand radical transfer route from XI to XIV can not be ruled out, but the electron transfer route would probably be favored by the considerable stability[4c] of the cation VI.[17]

[23] The marked increase in the yield of Schiemann product (III; Y = F) in proceeding from water to AcOH is readily explained by assuming that the diazonium salt exists to a much greater extent as intimate ion-pairs in AcOH than in water.[8]

TABLE 2. DECOMPOSITION PRODUCTS OF N,N-DIMETHYLBENZAMIDE-*o*-DIAZONIUM TETRAFLUOROBORATE

				Product yields (%)[a,b]					
						o-Subst.-N,N-dimethyl-benzamide, substituent =			
Solv.	Temp	Catalyst	Additive	Phthalimidine V; R = H	N–Me-benzamide VIII; R = H	H	OH	F	Cl
H_2O	70°			12·6	13·4	nil	72·4	1·6	—
H_2O	60°			12·5	13·5	nil	72·4	1·6	—
H_2O	40°			10·1	14·4	nil	73·6	1·9	—
H_2O	20°	Cu[c]		nil	99·7	0·3	nil	nil	—
H_2O	0°	Cu[c]		nil	98·9	1·1	nil	nil	—
H_2O	20°	Cu[c]	$Cu(NO_3)_2$[d]	nil	99·5	0·5	nil	nil	—
H_2O	20°	CuCl[e]		nil	99·6	0·4	nil	nil	nil
H_2O	20°	CuCl[e]	NaCl[f]	nil	91·9	1·0	nil	nil	7·1
H_2O	20°	CuCl[e]	NaCl[f] $Cu(NO_3)_2$[d]	nil	55·3	0·1	nil	nil	44·6
H_2O	20°	Cu_2O		nil	99·1	0·9	nil	nil	—
H_2O	20°	Cu	EDTA[g]	nil	98·3[k]	1·7[k]	nil	nil	—
AcOH	68°			19·6	10·0	nil	40·2[h]	30·2	—
AcOH	40°			16·0	12·1	nil	38·6[h]	33·3	—
AcOH	20°	Cu[c]		nil	32·3[h]	58·7	9·1[h]	nil	—
AcOH	20°	Cu[c]	H_2O[i]	nil	60·4[h]	35·6	4·0[h]	nil	—
AcOH	20°	Cu_2O[i,j]		nil	54·9[h]	37·9	7·2[h]	nil	—

[a] Determined by VPC. [b] Normalized to 100%; total recovery was 94–99% except where noted. [c] 3·2 g atoms/mole reactant. [d] 4 moles/mole reactant. [e] 1·1 moles/mole reactant. [f] 75 moles/mole reactant. [g] 1 mole/g atom of Cu. [h] After hydrolysis of acetate. [i] 1·2 moles/mole reactant. [j] Reacts with acetic acid to generate a mole of water per mole of oxide. [k] Total recovery was 65%.

external hydrogen atom source nor a ligand which can effectively be transferred as a radical is present.[24]

The products obtained when the copper catalyzed decomposition is carried out in acetic acid are also in good agreement with the reaction paths outlined in Scheme B. The formation of succinic acid along with, and in a quantity corresponding to that of, the unsubstituted tertiary amide (XII; R = H) provides strong evidence for the presence of radical intermediates.[25] It has not yet been determined whether the phenyl radical (X; R = H) or the rearranged radical (XI; R = H) is the species which abstracts the hydrogen atom from the methyl group of acetic acid to produce the N,N-dimethylbenzamide (XII; R = H).

The results in the copper induced decomposition of the N,N-dimethyldiazonium salt (I; R = H) in acetic acid support the contention that *all* the products of the thermal reaction are derived from phenyl cations. It could have been argued, *a priori*, that the hydrogen transfer product (VIII; R = H) from the thermal reaction is formed by the same route as that from the catalyzed reaction. Thus, the heterolytic

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[24] Evidence has been presented[4d] that the phthalimidine (V), produced in the thermal reaction, is formed by a direct attack of the phenyl carbonium ion on the α-carbon atom of the N-alkyl group rather than by an intramolecular electrophilic substitution in the cation VI. Insofar as N-methylphthalimidine (V; R = H) is not formed in the copper catalyzed reaction, in which the cation (VI; R = H) is probably present[22] as an intermediate in more significant quantities than in the thermal reaction, the present results support this mechanism for phthalimidine formation.

[25] M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.* **65**, 15 (1943).

decomposition of the diazonium ion in the thermal reaction could conceivably be in competition with a radical decomposition (leading to dealkylated product) induced by traces of copper present as an impurity in the solvent.[26] However, this possibility can be rejected because the radical path in acetic acid is seen to lead to a substantial degree of reduction resulting in the production of N,N-dimethylbenzamide (XII; R = H) whereas none of the latter is formed in the thermal reaction in the same medium.[27] The same type of conclusion can be reached in the case of the N-N-dibenzyl salt (I; R = C_6H_5), for the addition of thiophenol in the copper induced reaction produces the *t*-amide (XII; R = C_6H_5) while none of the latter is formed in the thermal reaction in the presence of the same additive, although N-benzylbenzamide (VIII; R = C_6H_5) is a major product.[4b] It is thus clear that the dealkylated product arises in the thermal reaction by a *hydride ion* transfer and in the catalyzed reaction from a *hydrogen atom* transfer.

It is of interest that N-methylbenzamide-N-methanol acetate (XIV; R = H) is produced rather than N-methylbenzamide (VIII; R = H) when this copper catalyzed decomposition is carried out in acetic acid under rigorously anhydrous conditions. It was detected in the product mixture by VPC and by IR spectroscopy (acetate carbonyl band at 1725 cm^{-1}). Hydrolysis of this mixture at room temperature with dilute acid converted this ester quantitatively into N-methylbenzamide (VIII; R = H) as determined by VPC and IR analysis.

Since no N,N-dimethylsalicylamide (XIII; Z = OH, R = H) could be detected when the copper catalyzed decomposition of I (R = H, X = BF_4) was performed in water, even in the presence of a large excess of cupric ions (added as cupric nitrate), it is clear that the ligand radical transfer[19] of H_2O^+ is considerably slower than the 1,5 hydrogen atom shift.[21] On the other hand, in the solvent acetic acid, ligand radical transfer of an acetoxy group is competitive with both intramolecular and intermolecular hydrogen atom transfer as is evident by the production of *o*-acetoxy-N,N-dimethylbenzamide (XIII; Z = OAc, R = H)[28] and its hydrolysis product (XIII; Z = OH, R = H) as well as N-methylbenzamide (VIII; R = H) and N,N-dimethylbenzamide (XII; R = H). This order of effectiveness in ligand radical transfer is in line with expectations based on other work.[18,30]

Cuprous chloride was next examined as a catalyst in this reaction, since ligand radical transfer of chlorine is known to be particularly efficient.[17,18] When used to catalyze the reaction of I (R = H, X = BF_4) in acetic acid, cuprous chloride is quite ineffective. However, in aqueous solution, it causes an extremely rapid reaction,

[26] Very small quantities of copper salts are capable of decomposing the *p*-nitrobenzenediazonium ion; E. S. Lewis and W. H. Hinds, *J. Amer. Chem. Soc.* **74**, 304 (1952).

[27] The extent of reduction of intermediate radicals (if any were present) would be even greater in the thermal than in the copper promoted reaction since the low concentration of cupric ions in the former case would decrease the effectiveness of the major competing process, ligand radical transfer, which yields phenol acetate.

[28] The amount of XIII (Z = OAc, R = H) formed in the Cu catalyzed experiments in AcOH was not reproducible and apparently depended on the rate of diazonium salt decomposition relative to the rate of formation of cupric acetate.[29]

[29] It was shown independently that when copper powder is treated with acetic acid a blue-green solution, which probably contains cupric acetate, is formed.

[30] The cupric ion concentration in the aqueous cupric nitrate run exceeded the upper limit of that of cupric acetate, attainable by complete conversion of the copper metal into cupric acetate.[29] Since Cu metal can be seen throughout the reaction, this conversion is clearly not complete.

leading to the same product as the copper catalyzed decomposition, namely, N-methylbenzamide (VIII; R = H).[31] None of the typical Sandmeyer product, *o*-chloro-N,N-dimethylbenzamide (XIII; Z = Cl, R = H) is formed in this case providing some indication of the rapidity of the intramolecular hydrogen atom transfer which occurs in preference to chlorine atom transfer.[12,13] In the presence of a 75 fold excess of chloride ion, added in the form of sodium chloride, hydrogen transfer still predominates and just a small amount (7·1%) of aryl chloride is produced.[32] Only when a four-fold excess of cupric salt is also added does ligand radical transfer compete effectively, leading to a 44·6% yield of Sandmeyer product.

Since cuprous chloride was found to promote the decomposition in water much more effectively than copper powder, it was suspected that univalent copper in general might be superior to the metal in this role. It has, in fact, been suggested that copper catalysis is merely due to the presence of cuprous copper on the surface of the metal.[13,33] When cuprous oxide was employed as a catalyst in the decomposition of I (R = H, X = BF_4) it was found to be extremely effective, causing instantaneous reaction and leading to the same products as copper powder catalysis in *both* water and acetic acid[34] solvents.

If cuprous ion on the surface of the metal is indeed the effective catalyst in copper promoted diazonium ion decompositions, the presence of a chelating agent should retard the reaction by effectively removing the catalyst; no such effect is expected if the metal itself functions as the catalyst. When the copper powder catalyzed decomposition of I (R = H, X = BF_4) was carried out in water containing an excess of the disodium salt of EDTA, the reaction rate was considerably reduced.[35] Consequently, catalysis by univalent copper seems to be suggested, without ruling out less effective catalysis by copper metal.[36]

CONCLUSIONS

These results provide strong evidence for the concept that copper catalyzed diazonium ion decomposition occurs by a radical process. They also suggest that cuprous ion, on the surface of the copper might be the active catalyst and that copper metal may be very advantageously replaced with cuprous oxide in such decompositions. These conclusions have significance with respect to the important class of ring closures known as Pschorr reactions[11] and we have utilized these concepts in unpublished work to induce unidirectional Pschorr reactions and quantitative reductions of diazonium ions.

[31] In a preliminary experiment, it was determined by Mr. L. D. McKeever that the cuprous chloride catalyzed decomposition of I (R = C_6H_5, X = HSO_4) in 2N H_2SO_4 in AcOH produces 80% N-benzylbenzamide (VIII; R = C_6H_5), 67% benzaldehyde and an unidentified tan oil. No ring closed products were found.

[32] It is believed that higher chloro complexes of copper (II) are more effective as chlorine atom donors than the lower complexes. See Ref. 12, footnote 5.

[33] J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry* p. 890. W. A. Benjamin, New York, N.Y. (1964).

[34] The product composition should be compared to that obtained in "wet" acetic acid since a mole of water is produced per mole of oxide.

[35] Whereas the reaction is usually over, under these conditions and without EDTA, after ca. 3 hr (as shown by a negative β-naphthol test) it required 15 hr to be complete in the presence of EDTA.

[36] A less likely possibility is that the EDTA, by complexing with ions on the metal surface, coats the latter making it inaccessible to the diazonium ion.

The results of the experiments with cuprous chloride provide support for the existence of phenyl radical intermediates and their consumption by ligand radical transfer in the Sandmeyer reaction.[12,13] In the present system the phenyl radical can undergo intramolecular hydrogen atom transfer in competition with ligand radical transfer and the latter mode of reaction is favored by high concentrations of cupric chloride.

Both 1,5-hydride ion[4a,37] and 1,5-hydrogen atom[38] transfers have been frequently observed, but this appears to be the first case in which either type, depending on the reaction conditions, can be made to occur in the same system. Thus, it might be possible for the first time to test theoretical predictions concerning the magnitude[39] and the sensitivity to substituent changes[40] of the isotope effects in hydride ion *vs.* hydrogen atom transfer reactions.

EXPERIMENTAL

M.ps were determined on a Kofler hot stage and they are corrected. The preparation of most of the compounds in the N,N-dibenzylbenzamide series and the thermal deamination method have been described.[4a,b] N,N-Dibenzylbenzamide was prepared by the method of Franzen.[41]

Copper catalyzed decomposition of N,N-*dibenzylbenzamide*-o-*diazonium hydrogen sulfate* (I; $R = C_6H_5$, $X = HSO_4$). To a solution of 5 mmoles of the diazotized salt[4b] in 30 ml 2N H_2SO_4 in AcOH at 23° were added 95 mg (1·5 mg atom) Cu-powder (Fisher Scientific). Immediate vigorous evolution of N_2 was observed; after 4 hr water was added and the reaction mixture was allowed to stand for another hr before work-up.[4b]

N,N-*Dimethylsalicylamide* (IV; S = H, R = H). A modification of the method of Coates[42] was used. A solution of 10·7 g (0·05 mole) phenyl salicylate (Eastman Kodak) and 14 g (0·08 mole) 25% aqueous solution of dimethylamine (Eastman Kodak) in 10 ml dioxan was placed in a glass lined stainless steel bomb and heated overnight on a steam bath. Extraction with CH_2Cl_2 yielded crude material contaminated with some phenol. Recrystallization from 95% EtOH gave 3·9 g (48%) white crystals, m.p. 162–163° (reported[43] m.p. 161–164°). Esterification with Ac_2O in pyridine yielded a liquid exhibiting IR absorptions at 1750 cm^{-1} (s), 1620 cm^{-1} (vs), 1150 cm^{-1} (m). NMR signals: τ 7·8 ppm (singlet, area 3), 6·2 ppm (singlet, area 3), 6·0 ppm (singlet, area 3), 2·7 ppm (multiplet, area 4).

o-*Amino*-N,N-*dimethylbenzamide* (XIII; $Z = NH_2$, R = H). The procedure described by Staiger and Miller[44] was used with only minor modifications. A 64% yield of the desired aminoamide (crude) was obtained when a 3:1 ratio of dimethylamine (Eastman Kodak 25% in water) to isatoic anhydride (Eastman Kodak) was used. Distillation at 124–125°/2 mm yielded a liquid which solidified to give a white solid, m.p. 38–39°. IR bands ($CHCl_3$): 3500 cm^{-1} and 3600 cm^{-1} (NH), 1620 cm^{-1} (CO). NMR signals (CCl_4); τ 7·1 ppm (sharp singlet, area 6), 5·4 ppm (broad, area 2), ca. 2·75 ppm (quartet, area 4).

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[37] B. J. Calvert and J. D. Hobson, *Proc. Chem. Soc.* 19 (1962); S. Winstein and R. L. Hanson, *J. Amer. Chem. Soc.* **82**, 6206 (1960).

[38] R. K. Freidlina, V. N. Kost and M. Y. Khorlina, *Russ. Chem. Rev.* (English Trans.) **31**, 5 (1962); H. Heusler and J. Kalvoda, *Angew. Chem.* (Intern. Ed. Engl.) **3**, 525 (1964); P. Kabashakalian, E. R. Townley and M. D. Yudis, *J. Amer. Chem. Soc.* **84**, 2716 (1962); P. Kabasakalian and E. R. Townley, *Ibid.* **84**, 2724 (1962).

[39] W. H. Saunders, *Technique in Organic Chemistry* (Edited by S. L. Friess, E. S. Lewis and A. Weissberger) Vol. VIII; Part 1, p. 389. Interscience, N.Y. (1961) and Refs cited there.

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N,N-*Dimethylbenzamide-*o*-diazonium tetrafluoroborate* (I; R = H, X = BF_4). Use of the usual procedure[3] gave an 80% yield of white needles, which could be kept in the freezer ca. 10 days without discoloration. IR bands (Nujol): 2255 cm^{-1} (N_2^+), 1630 cm^{-1} (s, CO), 1060 cm^{-1} (broad, BF).

o-*Chloro*-N,N-*dimethylbenzamide* (XIII; Z = Cl, R = H).[46] A solution of 3·13 g (0·02 mole) *o*-chlorobenzoic acid (Eastman Kodak) and 2·50 g (0·021 mole) $SOCl_2$ (Fisher Scientific) in 25 ml dioxan was heated at gentle reflux (110°) for 2 hr. After the solution had cooled to room temp, it was added, over a period of 10 min to 50 ml of a stirred 50% dioxan solution containing 0·1 mole dimethylamine [generated from the hydrochloride (Eastman Kodak) with NaOH]. Stirring was continued for 15 min and the solution was left overnight at room temp. Removal of the solvent at red. press. left a yellow oil which was extracted with dry ether. The combined ether extract was concentrated by distillation through an 8″ Vigreux column. Distillation at 96–97°/0·15 mm (reported[46] b.p. 157·5–159°/13·5–14 mm) yielded 3·12 g (85%) of a colorless liquid, the IR spectrum of which (neat) exhibited carbonyl absorption at 1642 cm^{-1}. NMR (neat): τ 7·3 ppm (singlet, area 3), 7·0 ppm (singlet, area 3) and ca. 2·7 ppm (multiplet, area 4).

o-*Fluoro*-N,N-*dimethylbenzamide* (XIII; Z = F, R = H).[45] This was prepared in the same way as the *o*-chloro isomer except that commercial *o*-fluorobenzoyl chloride (Pierce Chem. Co.) was used. A 55% yield of colorless liquid, b.p. 79–80°/0·15 mm, was obtained. The neat liquid exhibited a carbonyl band in its IR spectrum at 1642 cm^{-1} and the following NMR signals: τ 7·2 ppm (doublet, area 3),[47] 7·0 ppm (singlet, area 3) and ca. 2·7 ppm (multiplet, area 4).

Procedure for decomposition of diazonium tetrafluoroborates. Most of the reactions were replicated and were found to be completely reproducible except those performed in AcOH with Cu catalysis.[28] The products were found to be stable under the reaction conditions.

Thermal. A solution of 250 mg (1·00 mmole) of I (R = H, X = BF_4) in 30 ml distilled water was placed in an oil bath at the desired temp. When the evolution of gas had ceased and a β-naphthol test on a drop of solution was negative, the reaction mixture was saturated with NaCl and extracted several times with CH_2Cl_2. The combined extract was dried over $MgSO_4$ and concentrated. The same procedure was followed in AcOH except that prior to work-up the reaction mixture was poured into ca. 3 times its volume distilled water. Also, the combined organic extract was washed with sat $NaHCO_3$aq and water before drying.

Copper catalyzed. The procedure used was as in the thermal decomposition with the following modifications. The solution was thermostated at 20°, with stirring, and 200 mg (3·2 g atoms) Cu powder (Fisher Scientific) was added. Decomposition in the presence of excess cupric ions was carried out in a solution containing 1 g (4 mmoles) of cupric nitrate trihydrate (Baker and Adamson).

Cuprous chloride catalyzed. The usual procedure was followed, but 113 mg (1·10 mmole) of cuprous chloride (Fisher Scientific) was added instead of Cu powder. Decompositions in the presence of excess chloride ions were carried out in an aqueous solution containing 4·4 g (75 mmoles) NaCl and a few drops of 1N HCl.

Cuprous oxide catalyzed. The usual procedure was followed, adding 100 mg (0·7 mmole) cuprous oxide (Baker and Adamson) instead of Cu powder.

Gas chromatographic analysis. The product mixture was analyzed by VPC on a 4% polyphenyl ether column (on 70/80 Anakrom ABS) at 160° with a He flow rate of 50 ml/min. Naphthalene was used as internal standard and the thermal conductivities of all the products were calibrated *vs.* naphthalene.

Identification of succinic acid and N,N-*dimethylbenzamide* (XII; R = H) *in the copper catalyzed decomposition in acetic acid.* The usual procedure for Cu catalyzed decomposition in AcOH was followed, using 1·20 mmoles diazonium salt. However, all water washes were saved, combined and acidified with conc. HCl. This solution was distilled through a Vigreux column, most of the material coming over at 100°. The green solution was distilled to dryness at red. press. leaving a green residue to which a little D_2O and anhydrous K_2CO_3 were added. The color changed to aqua blue. The blue solid was separated from the water white liquid by centrifugation. The NMR spectrum of the solution (on a Varian A-60 spectrometer) showed a sharp single line 141 c/s upfield from the water signal. (Control solutions showed that the succinic acid resonance also occurs 141 c/s upfield from

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[45] We wish to thank Dr. Jonathan Lipowitz for the preparation of this compound.

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water; acetic acid absorbs 173 c/s upfield from water under the same conditions.) The solvent was removed from this solution and the solid which remained was combined with the blue solid from above. The solids were treated with a small amount of dil H_2SO_4. The residue remaining after evaporation of the solvent was leached with EtOH. Evaporation of the EtOH left 32 mg (0·29 mmole) of a white solid, m.p. 180–190°, undepressed when admixed with an authentic sample of succinic acid.

VPC analysis of the organic extracts indicated a 50% yield (0·60 mmole) N,N-dimethylbenzamide. The retention times on a polar and a non-polar column were identical to those of an authentic sample (Fisher Scientific). IR evidence for the structure of this amide was obtained by analysis of the product from another run (*vide infra*).

Detection of N-*methylbenzamide*-N-*methanol acetate* (XIV; R = H). Decomposition of N,N-dimethylbenzamide-*o*-diazonium tetrafluoroborate was carried out under strictly anhydrous conditions. At the end of 2 hr, the solution was subjected to distillation under red. press. in order to remove the AcOH. As the volume decreased, *o*-dichlorobenzene was added and the distillation was continued until no more AcOH came over. Analysis of the liquid part of the residue by VPC showed its composition to be 52% N,N-dimethylbenzamide, 6% *o*-acetoxy-N,N-dimethylbenzamide and ca. 42% of a new material. IR analysis of this mixture showed carbonyl absorptions at 1625 cm^{-1} (vs, tertiary amide), 1760 cm^{-1} (m., phenolic acetate) and 1725 cm^{-1} (s., aliphatic acetate). When an aliquot of this mixture was treated with 5% H_2SO_4 at room temp, the new material could no longer be detected by VPC. Instead, the mixture now consisted of 52% N,N-dimethylbenzamide, 3% *o*-acetoxy-N,N-dimethylbenzamide, 2% N,N-dimethylsalicylamide and 43% N-methylbenzamide. Examination of the IR spectrum indicated that the aliphatic ester band at 1725 cm^{-1} had been replaced with another at 1660 cm^{-1} (s, carbonyl group of N-methylbenzamide). The relative intensities and frequencies of the several carbonyl bands were consistent with the composition of the mixture as determined by the VPC analysis.