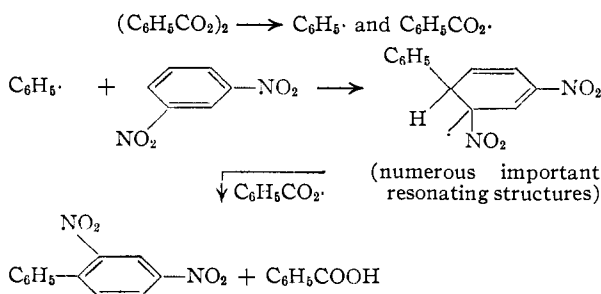


2,4-dinitrophenyl formed by benzoyl peroxide phenylation of 2,4-dinitrotoluene with that calculated assuming no isotope effect is in accord with expectation if the phenylation occurred by mechanism 2. Mechanism 1 would have predicted a substantial isotope effect. We therefore conclude that, at least for the free radical phenylation of *m*-dinitrobenzene, the mechanism is clearly established as involving intermediate addition of the



phenyl radical to the dinitrobenzene, followed by a non-rate controlling loss of hydrogen.

It should be pointed out that the mechanism demonstrated for the case of phenylation of *m*-dinitrobenzene may not necessarily hold for attack on less activated aromatic rings. For example, where resonance stabilization for the intermediate radical adduct with two groups as favorable for radical stability as the two nitro groups in *m*-dinitrobenzene is absent, radical abstraction could become more important. Such a mechanism would be particularly favored for a radical like the hydroxyl radical^{2b} because of the contribution of the very strong hydrogen-oxygen bond that would be formed in the process.

Acknowledgment.—The authors wish to express their appreciation to Dr. R. C. Anderson and colleagues at Brookhaven National Laboratory, whose cooperation made this work possible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

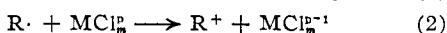
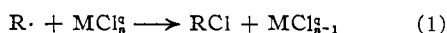
The Mechanism of the Sandmeyer and Meerwein Reactions

BY JAY K. KOCHI*

RECEIVED SEPTEMBER 4, 1956

The Sandmeyer and Meerwein reactions are postulated to proceed *via* a common aryl radical. Reaction of the aryl radical with metal halide or its addition to olefin followed by reaction with metal halide gives Sandmeyer or Meerwein products, respectively. Evidence is given for the existence of aryl and aralkyl radicals and for the radical chain termination properties of metal halides. By utilizing these reactions, Sandmeyer and Meerwein products are obtained from sources other than arenediazonium salts.

Previous kinetic studies of the Sandmeyer¹ and related Meerwein² reactions have shown that these reactions are first order in both diazonium ion and cuprous salt, but they have not given complete information on the mechanisms of these reactions. We wish to give evidence for a common mechanistic path involving free radical intermediates. The essential feature of this mechanism is the role of the metal ion (copper) in acting as an effective radical chain terminator.³ In the case of the two metal ions we studied (copper and iron), the process can be formulated as



These processes represent alternate routes by which radicals can react with metal and complex-metal ions; that is, (1) directly through a ligand bridge or (2) *via* an electron transfer process.^{4,5} In the

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(1) W. Cowdrey and D. Davies, *J. Chem. Soc.*, S48 (1949).

(2) J. K. Kochi, *THIS JOURNAL*, **78**, 1228 (1956).

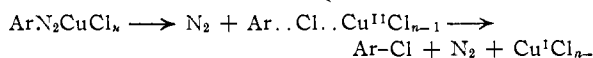
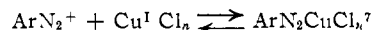
(3) C. Bamford, A. Jenkins and R. Johnston, *Nature*, **177**, 992 (1956); F. Dainton and E. Collinson, *ibid.*, **177**, 1224 (1956); J. K. Kochi, *THIS JOURNAL*, **78**, 4815 (1956).

(4) The various aspects of these transfers have been elegantly presented by Taube and co-workers (H. Taube, *et al.*, *THIS JOURNAL*, **75**, 4119 (1953); **76**, 2103 (1954); **76**, 4053 (1954); **77**, 4481 (1955)).

(5) The cupric ion alone is not wholly sufficient for its ability to act as a chain terminator. It appears that the most efficacious species is a higher chloro-complex, probably CuCl_3 . Thus, our experiments (*vide infra*) indicate that in the presence of limited chloride ions, an

Sandmeyer reaction aryl radicals react predominantly by equation 1, whereas with alkyl radical produced in the Meerwein reaction, processes 1 and 2 sometimes appear to be competitive.

Sandmeyer Reaction.—The free radical nature of the Sandmeyer reaction has been most consistently advocated by Waters^{6a} and more recently by Pfeil,^{6b} who postulate a quasi-intramolecular reaction involving one-electron transfers as

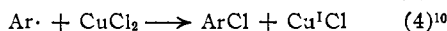
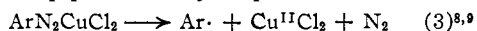


The important characteristic of this mechanism is the unique role played by cuprous ion in an oxidation-reduction capacity. We believe that it is *not* appreciable number of aryl radicals react by dimerization, while high chloride ion concentrations enhance the yields of Sandmeyer product (*cf.* references 1, 9b and 35).

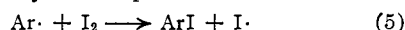
(6) (a) W. Waters, "Chemistry of Free Radicals," 2nd Ed., Oxford Univ. Press, London, 1948, p. 163. (b) E. Pfeil and O. Velten, *Ann.*, **562**, 163 (1949); **565**, 183 (1949).

(7) Most mechanisms of the Sandmeyer reaction involve the intermediate formation of a diazonium-cuprous complex. This postulate is based partially on the observed formation of a colored complex when gross amounts of diazonium and cuprous salts are mixed. Whether these represent true intermediates has not been rigorously shown. For a discussion regarding the nature of these complexes see references 6b and 19a. It is not important for the purposes of what follows whether the reaction proceeds (a) through the rapid reversible formation of a complex intermediate followed by its slow decomposition or (b) by a slow bimolecular reaction of the diazonium ion and cuprous salt (see footnote 38). The contrary notwithstanding we shall treat the reaction as proceeding by the former path.

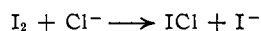
essential that this process be cyclic; instead a discrete two-step process may be postulated



Our experiments indicate that free aryl radicals are present in the catalyzed decomposition of diazonium ions (equation 3). For example, when *p*-nitrobenzenediazonium chloride is decomposed in aqueous acetone solutions with cuprous chloride in the presence of iodine, iodine is consumed rapidly to give good yields of *p*-nitroiodobenzene

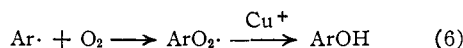


The possibility that the iodo compound is formed by an ionic process involving iodide ion formed by reactions such as



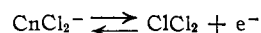
is made unlikely by the greater than 100% yields of *p*-nitroiodobenzene based on one mole of product per mole of iodine taken. Furthermore, any iodide formed in such reactions would probably be oxidized rapidly by the cupric ion.

When *p*-nitrobenzenediazonium bisulfate is treated with cuprous chloride in the presence of limited amounts of chloride ions in aqueous acetone solutions at -25° in the presence of oxygen, in addition to a 42% yield of *p*-nitrochlorobenzene a 46% yield of *p*-nitrophenol is obtained.



In the absence of oxygen, cupric sulfate also precipitates from solution and *p*-nitrochlorobenzene and 4,4'-dinitrobiphenyl¹² can be isolated in 76 and 9% yields, respectively. In the presence of excess cupric chloride the formation of the Sandmeyer product is increased at the expense of the coupling product.¹³ Further substantiation of the

(8) Transient aryldiazo radicals may be formed. The significance of a particular chlorocuprous ion, CuCl_2^- , as the catalyst¹ in the Sandmeyer reaction, in this scheme, can be attributed to the favorable half-cell potential



compared to the other chlorocuprous ions. (See, for example, N. Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1950, p. 103 ff.)

(9) (a) S. Dickerman, K. Weiss and A. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); (b) W. Waters, private communication (see also D. Nonhebel and W. Waters, Abstracts, International Congress on Catalysis, Philadelphia, Pa., 1956.)

(10) Aryl radicals appear to react by process 1 which involves a direct halogen atom transfer to form the aryl halide. The alternative two-step process is an oxidation to an arylcarbonium ion followed by reaction with halide ion. This latter route appears untenable in view of the absence of phenols when the reaction is obtained in water as solvent. If carbonium ions were intermediates, phenols would be expected since arylcarbonium ions obtained in the ionic unimolecular solvolysis of aryldiazonium ions show little selectivity¹¹ for nucleophiles.

(11) E. Lewis and W. Hinds, *THIS JOURNAL*, **74**, 304 (1952); D. DeTar, *et al.*, *ibid.*, **76**, 1680 (1954); **72**, 865 (1950).

(12) W. Waters ("Chemistry of Free Radicals," 2nd Ed., Oxford Univ. Press, London, 1948, p. 165) postulates that biaryls arise by the coupling of aryl radicals (see, however, reference 19).

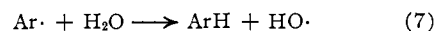
(13) That the *p*-nitrophenyl radical may not react instantaneously with oxygen is indicated by the small amount of 4,4'-dinitrobiphenyl which is obtained in the oxygen run. The yield of the biaryl appears to be proportional to the rate of addition of cuprous chloride. The precedent for this deduction appears in the works of Walling and Buckler and Muller and Topel who obtained appreciable amounts of

production of aryl radicals under these conditions is the report of Dickerman, *et al.*,^{9a} that aromatic solvents can be arylated. Waters and Nonhebel^{9b} have been able to polymerize acrylonitrile in aqueous solutions under the conditions of the Sandmeyer reaction in the absence of oxygen. Aryl residues as end-groups were accounted for in good yields.

Systems other than arenediazonium and cuprous salts give indications of the chain-terminating properties of metal halides. For example, *p*-nitrochlorobenzene is formed in 84% yield from the decomposition of *N*-nitroso-*p*-nitroacetanilide in acetone solutions of ferric chloride. Chlorobenzene and trityl chloride are formed by a similar decomposition of phenylazotriphenylmethane in the presence of ferric chloride. Analogously, azobisisobutyronitrile produces significant amounts of cuprous chloride when it is decomposed in anhydrous *t*-butyl alcohol containing cupric chloride.^{17a} Under similar conditions in acetonitrile, the rate of formation of cuprous chloride was found to be zero order in cupric chloride.^{17b} The use of cupric salts as inhibitors of vinyl polymerization also points to their effectiveness as radical chain terminators.

That cupric chloride reacts with aryl radicals under the usual Sandmeyer conditions was shown by Pfeil and Velten^{6b} who obtained quantitative yields of *p*-nitrochlorobenzene when aqueous solutions of *p*-nitrobenzenediazonium bisulfate were treated with sufficient quantities of cupric chloride at 100° . Furthermore, Leonhards¹⁸ has shown that the addition of cupric chloride greatly reduced the amount of cuprous chloride required in the aqueous Sandmeyer reaction from as much as 0.2 to only 0.01 mole.

In aqueous solutions the destruction of the aryl radicals can occur by several competitive paths: (1) dimerization to yield biaryl,¹⁹ (2) reaction with diazonium ion and cuprous salt to give azo compound¹⁹ and (3) reaction with cupric chloride to give the Sandmeyer product. The solvent water does not appear to react significantly by the energetically less favorable process²⁰



biphenyl in addition to phenol in the oxygenations of Grignard and lithium reagents, respectively.¹⁴ Wieland, furthermore, reported that some biphenyl is obtained when phenylazotriphenylmethane is decomposed in the presence of oxygen¹⁵ (*cf.* references 16). See further for indications of the selective reactions of radicals with oxygen.

(14) C. Walling and S. Buckler, *THIS JOURNAL*, **77**, 6032 (1955); E. Muller and T. Topel, *Ber.*, **72B**, 273 (1939).

(15) H. Wieland, *Ann.*, **514**, 145 (1934).

(16) J. Baxendale and J. Magee, *Disc. Faraday Soc.*, **14**, 160 (1953); D. DeTar and M. Turetzky, *THIS JOURNAL*, **76**, 3928 (1956).

(17) (a) Unpublished results with R. Keys; (b) J. Kumamoto, private communication.

(18) W. Leonhards, Doctoral Dissertation, Marburg, Germany, 1952.

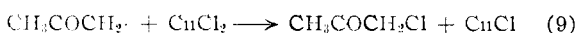
(19) (a) E. Pfeil, *Angew. Chem.*, **65**, 155 (1953). (b) An alternative route for the diaryl formation in Sandmeyer type reactions may be *via* intermediate aryl copper compounds which may arise from the reaction of aryl radicals with cuprous chloride. Aryl copper compounds are known to undergo such decomposition to diaryls (H. Gilman, "Organic Chemistry," 2nd Ed., Vol. I, J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 542). Similarly, it is possible for azo compounds to result from the reaction of these nucleophilic aryl copper compounds with diazonium salts. These alternatives must be held with a certain amount of reserve since aryldimethylcarbinols are not isolated when acetone is used as solvent.

(20) Rather the reverse process is obtained (J. Baxendale and J. Magee, *Trans. Faraday Soc.*, **51**, 204 (1955)).

In aqueous acetone solution, however, appreciable amounts of reduction (*i.e.*, chain transfer) by solvent²¹ does take place to produce a more stable acetylonyl radical



The resulting acetylonyl radicals can either dimerize²³ or react with cupric chloride to form chloroacetone. The yields of the reduction product, ArH, are found to be approximately equal to the chloroacetone formed.⁹



In order to assess the efficiency with which cupric chloride reacts with aryl radicals, the relative amounts of reduction to substitution (equations 8 and 4) were measured by determining the amount of chloroacetone formed as a function of the cupric chloride concentration. Aqueous acetone solutions containing diazonium salt, cupric chloride and sealed breakable ampules of cuprous chloride were carefully degassed. The amounts of cuprous chloride remaining and chloroacetone formed were determined quantitatively after the diazonium decomposition was complete. As shown in Table I

TABLE I
EFFECTS OF CUPRIC CHLORIDE AND OLEFIN ON CHLOROACETONE FORMATION AND CUPROUS CHLORIDE CONSUMPTION^a

Benzenediazonium chloride	Run	Cupric chloride, meq.	Chloroacetone, ^b meq.	Cuprous ^c chloride, meq.
2,4-Dichloro	1	0	0.68	0.0157
	2 ^d	0	.12	.0690
	3 ^e	0	.095	.0724
	4	0.88	.51	.0994
	5 ^e	0.88	.10	.107
	6	7.04	.24	.116
Unsubstituted	7	0	.78	
	8 ^d	0	.11	
	9 ^e	0	.12	
	10	7.04	.19	
	11 ^e	7.04	.17	
4-Chloro	12 ^f	0	.73	
	13	0	1.02	
	14 ^g	0	1.60	
	15 ^d	0	0.11	

^a In acetone (25 ml.) containing 2.84 meq. of diazonium salt, 18.60 meq. of chloride, 0.128 meq. of cuprous chloride and 8 ml. of water at 0°. ^b Total chloroacetone formed, including reaction between cupric chloride and acetone (in most cases negligible at these temperatures). ^c Cuprous chloride remaining after completion of reaction. ^d Contains 25 meq. of acrylonitrile. ^e Contains 25 meq. of styrene. ^{f,g} Contains 1.42 meq. and 5.42 meq. of diazonium salt, respectively.

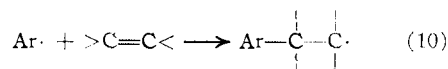
the reduction of aryl radicals (as measured by the chloroacetone formed) can be effectively decreased by increasing the amount of added cupric chloride (*cf.* runs 1, 4 and 6; 7 and 11; 12, 13 and 14). It is apparent, moreover, that with increasing cupric chloride concentration less cuprous chloride is consumed, as would be expected from the preceding argument.

(21) It has been reported^{2b} that the Sandmeyer reaction in methanol produces no formaldehyde.

(22) W. Waters, *J. Chem. Soc.*, 2007 (1937); 864, 1805 (1939).

(23) In none of our experiments could we find acetylacetone.

Meerwein Reaction.—In the presence of olefin, aryl radicals produced from diazonium salts by cuprous chloride in a process such as (3), undergo a third important reaction, *viz.*, addition



In all cases known, the direction of addition to an unsymmetrical olefin corresponds to that producing the more stable radical.²⁴ In a subsequent reaction the aralkyl radical²⁵ can react with metal ion by either of the steps postulated previously (equations 1 and 2); *i.e.*, by a direct transfer of a halogen atom from copper to the radical or by an oxidation to a carbonium ion.²⁷ These two competitive processes are illustrated by the reaction of phenyl and *p*-nitrophenyl radicals with styrene. In the former case the exclusive product is α -chlorobibenzyl (equation 1); with the *p*-nitrophenyl radical, on the other hand, a mixture of α -chloro-*p*'-nitrobibenzyl and *p*-nitrostilbene is obtained. Under the conditions of the experiment the chloride does not eliminate to yield olefin. It is not quite certain at present whether the reactions of metal ions with radicals by these two processes involve the same complexed metal ion^{4b} (*i.e.*, $m = n$). There is some evidence that the metal ion involved in the direct halogen transfer step is in a higher chloro-complex form than that involved in the electron transfer step. For example, when *p*-nitrobenzenediazonium bisulfate is decomposed in aqueous acetone solution containing styrene with cuprous chloride (*i.e.*, a limited amount of chloride ion present) a 21% yield of *p*-nitrostilbene is formed. The same reaction with an excess of chloride ion produces only 9% stilbene.

The presence of aralkyl radicals in the chain propagation step (equation 10) is shown by the trapping of this radical by iodine and oxygen. If iodine is added to a cuprous-catalyzed decomposition of *p*-nitrobenzenediazonium chloride in the presence of acrylonitrile, the intermediate hydro-

(24) (a) C. Koelsch and V. Boekelheide were the first to point out the free radical nature of this reaction (*THIS JOURNAL*, **66**, 412 (1944); **65**, 57 (1943)); (b) *Cf.* R. Huang, *J. Chem. Soc.*, 1749 (1936).

(25) O. Vogl and C. Rondstedt²⁶ have shown in the case of the maleic-fumaric acid system that the addition to the double bond is not stereospecific, which indicates that the aralkyl radical is "free."

(26) O. Vogl and C. Rondstedt, *THIS JOURNAL*, **78**, 3799 (1956).

(27) (a) Previous workers²⁸ have shown how it is possible for the carbonium ion to eliminate a β -proton or a β -carboxyl group to form olefins. (b) A case can be made, however, for the olefins to be formed from the aralkyl radicals by direct removal of the β -hydrogen atom by either cupric chloride or another radical. There is no precedent for cupric chloride acting in this capacity (see however reference 9 and 29). The removal of the β -hydrogen atom by radicals is analogous to the mechanism of homolytic aromatic substitution.³⁰ It is interesting to note that Vogl and Rondstedt (reference 31) obtained phenylated coumarins, albeit in low yields, from aryl radical sources in the absence of metal ions. That the low yield is not due to the unreactivity of aryl radicals formed under these different conditions is borne out by the fact that the starting coumarin is isolated in poor yield. Instead it appears that the aralkyl radical resulting from the attack on coumarin disappears by reaction with solvent and/or reactants.

(28) H. Meerwein, E. Buchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1939); R. Fusco and S. Rossi, *Gazz. chim. ital.*, **78**, 521 (1948).

(29) J. Kochi, *THIS JOURNAL*, **77**, 5274 (1955).

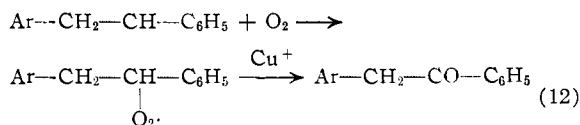
(30) D. Hey and G. Williams, *Disc. Faraday Soc.*, **14**, 216 (1953); W. Waters, M. Szwarc, J. Baxendale, A. Bickel, F. Mayo, *etc.*, *ibid.*, pp. 246 ff.

(31) C. Rondstedt and O. Vogl, *THIS JOURNAL*, **77**, 3067 (1955).

cinnamionitrile radical is trapped as the iodide



In a like manner *p*-nitrobenzenediazonium bisulfate and styrene do not react with cuprous chloride and oxygen at -25° to form Meerwein product. Instead the aralkyl radical reacts with oxygen to form an intermediate peroxide which in the presence of cuprous ion is reduced³² to the ketone, *p*-nitrode-soxybenzoin



It is interesting to note that under these latter conditions no phenol is formed. It appears, thus, that the *p*-nitrophenyl radicals react preferentially with styrene rather than oxygen.¹³

That the intermediate aralkyl radicals react with metal halides in a chain-terminating step corresponding to equations 2 and 1 to yield Meerwein products is shown by the reaction of compounds other than diazonium salts. Thus, the *p*-nitrophenyl radical obtained by decomposing *N*-nitroso-*p*-nitroacetanilide in anhydrous acetone solutions of ferric chloride and styrene yield α -chloro-*p*'-nitrobibenzyl in 43% yield. With acrylonitrile, α -chloro-*p*-nitrohydrocinnamionitrile is formed in 15% yield. Similarly phenylazotriphenylmethane under the same conditions yields α -chlorobibenzyl in 46% yield. Based on the carbon dioxide liberated (20% of the benzoyloxy radicals) benzoyl peroxide gives 54% α -chlorobibenzyl. The remainder of the benzoyloxy radicals are accounted for as benzoic acid (52%) and $\text{C}_6\text{H}_5\text{CO}-\text{CH}_2-\text{CHCl}-\text{C}_6\text{H}_5$ (24%). The latter product corresponds to the addition of benzoyloxy radicals to styrene followed by the usual chain termination by ferric chloride as in equation 1.

Reactions of Aryl Radicals.—These experiments indicate three principal modes by which aryl radicals formed under the conditions of the Meerwein reaction react: (1) reaction with solvent acetone leading to reduction to ArH and to formation of an equivalent amount of chloroacetone, (2) direct reaction with metal halide to form Sandmeyer product and (3) addition to olefin to yield a Meerwein product. The nature of the competition between the first two reactions (equations 1 and 4) already has been shown. That between the latter two, *viz.*, reaction of aryl radicals and olefin or metal halide was shown previously during a kinetic study of this reaction.² With increasing cupric concentration it was found that the yield of Meerwein product *decreased* in favor of the competing Sandmeyer reaction as indicated by equations 10 and 4. Similarly as shown in Table I the amount of chloroacetone formed (corresponding to reduction of aryl radicals) is markedly decreased by the presence of olefin (*cf.* runs 1, 2 and 3; 7, 8 and 9) at the usual cupric levels, indicating that these olefins are able to compete effectively with the solvent for aryl radicals (equation 10 and 8).

(32) M. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 129 (1951).

The rate of the reaction (as measured by the rate of the diazonium decomposition) as a function of olefin has been the source of considerable difficulty in interpreting^{24a,26,33} the mechanism of the Meerwein reaction. Qualitative experiments have indicated that the rate is a function of the structure of the olefin. We had shown earlier² that at high cupric concentrations the rate of nitrogen evolution is essentially independent of the acrylonitrile concentration. At low cupric and high olefin concentrations the rate approached a limiting value. In the latter case by further kinetic studies we have shown that the rate of nitrogen evolution is essentially independent of the olefin, at least with the two rather unrelated³⁴ alkenes, styrene and acrylonitrile. We have also re-examined the rates of the reactions at *low olefin* and *low cupric* concentrations (where it was shown earlier that low rates were obtained) and find that the *decrease in the rate is due to the extraneous consumption of cuprous catalyst*. In these experiments cuprous chloride was generated *in situ* by the relatively slow reaction of cupric chloride and acetone.²⁹ In Table II, experiments labeled with superscripts (*d*) contain no diazonium salt and represent those in which the maximum attainable cuprous salt concentrations are obtained with various amount of cupric chloride. The decreases in cuprous titer from these values are shown as a function of cupric and olefin concentrations. It is seen that at low cupric concentrations (*cf.* runs 1 and 2) there is an appreciable consumption of cuprous catalyst by the decomposing diazonium ion, while at high cupric concentrations (runs 11 and 12) the disappearance of cuprous catalyst is not detectable. The addition of olefin to these systems has the effect of profoundly affecting the rate of diazonium decomposition and cuprous titer at low cupric levels (runs 2, 3 and 4); at high cupric con-

TABLE II

RATE OF DIAZONIUM DECOMPOSITION AND CUPROUS CHLORIDE FORMATION

Run	Cupric ^a nitrate, meq.	<i>k</i> app., ^b ml./min.	Cuprous ^c chloride, meq.
1	0.352 ^d	..	0.0079
2	.352	1.7	.0055
3	.352 ^e	2.7	.0069
4	.352 ^f	2.8	.0071
5	.830 ^d	..	.011
6	.830	2.6	.0095
7	.830 ^e	3.1	.010
8	.830 ^f	3.1	.010
9	1.76 ^d	..	.017
10	1.76	3.5	.016
11	3.52 ^d	..	.026
12	3.52	3.5	.026
13	3.52 ^f	3.6	.026

^a In acetone (15 ml.) containing 1.42 meq. of *p*-chlorobenzenediazonium chloride, 8.5 meq. of lithium chloride and 8 ml. of water at 25°. ^b Measured as rate of nitrogen evolution at 35% reaction (see reference 2). ^c Cuprous chloride formed in 19 minutes. ^d Contains no diazonium salt. ^e Contains 4 meq. of acrylonitrile. ^f Contains 4 meq. of styrene.

(33) W. Bruner and H. Perger, *Monatsh.*, **79**, 187 (1948).

(34) P. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, pp. 178 ff.

centration (*cf.* 12 and 13) neither the rate of diazonium decomposition nor cuprous titer are affected. The yields of Sandmeyer and Meerwein products, however, are markedly different in each case as was shown previously.²

It is apparent that at low cupric and low olefin concentrations the bimolecular reaction of aryl radicals and olefin or metal halides is subverted by reactions involving consumption of cuprous catalyst (*e.g.*, dimerization of radicals or azo compound formation). Since the reaction in aqueous acetone is extremely sensitive to cuprous catalysts,³⁵ a small decrease in catalyst concentration due to these catalyst-destroying reactions would lead to significant changes in rate of diazonium decomposition. At low cupric, but high olefin concentrations, the olefin effectively competes with cuprous-consuming reactions as shown by the unchanged cuprous titer.

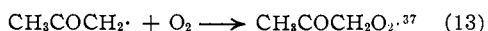
Thus, the observed qualitative variation in rates of diazonium decomposition with various olefins can be attributed to the efficiency with which each olefin competes with oxygen³⁶ and other side reactions which destroy catalyst. Although earlier mechanisms involving various forms of olefin complexation cannot be entirely discounted on the basis of these results, they appear to be unnecessarily involved.

The role of acetone in the decomposition of diazonium salts is threefold: (1) reaction with cupric chloride to produce cuprous chloride,²⁹ (2) solvent effects favoring higher chloro-complexes of cuprous and cupric ions^{5,29} and (3) acceleration of the bimolecular reaction of diazonium and complex cuprous ions.³⁸ It is not necessary, moreover, that acetone acts in the first capacity since it is known that diazonium acetates and chlorides can be decomposed to give aryl radicals,⁴⁰ which can react with cupric chloride in a subsequent step (equation 4) to produce autocatalytic reactions. The essential requirement of the solvent, however, is that it does not effectively compete with olefin or metal halides for the aryl or aralkyl radicals in chain-terminating processes.

The unique feature of metal halides in acting as chain-terminating agents is the efficiency and selectivity with which they react with radicals. Thus, it is well known that olefins are not polymerized to any appreciable extent under the conditions of the Meerwein reaction despite the presence of radicals such as aryl and aralkyl which are known chain initiators. The selectivity with which metal halides

(35) J. Kochi, *THIS JOURNAL*, **77**, 5090 (1955).

(36) Previous workers have taken little pains to eliminate oxygen from their reactions. The retardation of the Meerwein and Sandmeyer reactions by oxygen³⁵ is now accounted for by reactions which destroy cuprous catalyst such as equations 5, 6 and 13 in addition to the direct oxidation of the cuprous ion.



(37) I. Kolthoff and A. Medalia, *THIS JOURNAL*, **71**, 3784 (1949).

(38) Other solvents can serve the latter two purposes with varying degrees of efficacy. Thus, lower alcohols, dimethylformamide, acetonitrile, etc., increase the rate of reaction between these oppositely charged species. Similarly, the ionic reaction of iodide ion and diazonium ion is extremely rapid in acetone, alcohol and dioxane solutions.³⁹

(39) Unpublished results.

(40) W. Waters, *ref. 12*, p. 148 ff.

react with aralkyl radicals (such as growing styryl and acrylonitrile radicals) may be interpreted in terms of the life-times (reactivities)⁴¹ of these radicals in solution. This speculation must be subjected to further scrutiny.

Acknowledgments.—I would like to thank Dr. George S. Hammond for generous research facilities and the Institute for Atomic Research, Ames Laboratory, for numerous infrared spectra.

Experimental

Sandmeyer Reaction. Decomposition of *p*-Nitrobenzenediazonium Chloride.—A stock solution of *p*-nitrobenzenediazonium chloride was made by diazotizing 69 g. (0.5 mole) of *p*-nitroaniline with 108 ml. of concentrated hydrochloric acid, 200 g. of ice and 35 g. of sodium nitrite in 100 ml. of water. Excess nitrite was destroyed with urea and the clear filtered solution made up in 500 ml.

(a) **Oxygen-free.**—A 125-ml. portion of this stock solution was added to 500 ml. of acetone in a round-bottom flask at 0°. Oxygen-free argon was swept through the solution and a solution containing 2.0 g. of cuprous chloride and 1 g. of lithium chloride in 50 ml. of anhydrous acetone was added dropwise. Nitrogen was evolved immediately. Vacuum distillation of the acetone, followed by ether extraction, yielded 13.6 g. (68%) of *p*-nitrochlorobenzene (m.p. 82–84°). The mother liquors yielded 21% nitrobenzene.

When another 125-ml. portion of the diazonium solution was subjected to the same treatment except for the addition of 26 g. (0.2 mole) of cupric chloride, 82% *p*-nitrochlorobenzene and 9% nitrobenzene were isolated. Much less cuprous solution was needed for this reaction.

(b) **With Iodine.**—To a similar deoxygenated mixture was added a solution of 10 g. (0.039 mole) of iodine in 150 ml. of acetone, followed quickly by an acetone solution containing 5 g. of cuprous chloride and 3 g. of lithium chloride. The nitrogen evolution was instantaneous and a heavy precipitate of *p*-nitroiodobenzene formed. The solution was diluted with water and filtered. The extraction of the dried solid with ether leaves nearly pure *p*-nitroiodobenzene; the ether extracts lead to a 44% (8.7 g.) yield of *p*-nitrochlorobenzene. No nitrobenzene could be detected. The combined yields of *p*-nitroiodobenzene after crystallization (ligroin, m.p. 171–173°) and careful work-up of the mother liquors is 15.6 g. (162% based on I₂). The original acetone solution darkened on standing due to the oxidation of the hydrogen iodide. It is necessary that the cuprous solution follow soon after the addition of the iodine since there appears to be a slow reaction between diazonium salts and iodine in acetone solutions (*vide infra*).

With 5 g. of iodine a 178% yield (based on I₂) of *p*-nitroiodobenzene and a 65% yield of *p*-nitrochlorobenzene (based on diazonium salt) is obtained. Similarly, 23 g. of iodine gives a 93% yield of the iodo compound (based on the diazonium salt).

Decomposition of Diazonium Bisulfates (Minimum Chloride). (a) **Oxygen-free.**—Crystalline *p*-nitrobenzenediazonium bisulfate (NBDB)⁴² (12 g., 0.0485 mole) was dissolved in 40 ml. of water and added to 400 ml. of redistilled acetone. Purified argon was bubbled through the chilled solution (–25°) and an anhydrous acetone solution of cuprous chloride (10 g.) and lithium chloride (7 g.) was added slowly to the anaerobic solution. The solution, after nitrogen evolution was complete, was decanted from the precipitated cupric sulfate and vacuum distilled at room temperature. Water was added to the residue and the mixture extracted with ether. Evaporation of the ether left 6.5 g. of solid residues which consisted of 5.7 g. (76%) of *p*-nitrochlorobenzene and 0.54 g. (9.1%) of 4,4'-dinitrobiphenyl (m.p. 233–235°). Nitrobenzene could be detected in the mother liquors.

This reaction was repeated with the addition of 10 g. of cupric chloride. Much less cuprous chloride was required for complete nitrogen evolution, and the yield of *p*-nitrochlorobenzene was 85%, and only 3% of the biphenyl compound was isolated.

(41) M. Kharasch, E. Simon and W. Nudenberg, *J. Org. Chem.*, **18**, 329 (1953).

(42) J. Kochi, *THIS JOURNAL*, **77**, 3208 (1955).

(b) **With Oxygen.**—Oxygen was bubbled through a chilled (-25°) solution containing 10.8 g. of NBDB, 50 ml. of water and 400 ml. of acetone. A solution of cuprous chloride (7 g.) was added slowly over a period of several hours while oxygen was bubbled vigorously through the solution under slight pressure (5 p.s.i.). Acetone was vacuum distilled from the decanted solution at room temperature and the residue extracted with chloroform. The dried chloroform solution (sodium sulfate) yielded 5.8 g. of solid residue. Extraction with petroleum ether gave 2.9 g. (42%) of *p*-nitrochlorobenzene. Sublimation of the residue resulted in 2.8 g. (46%) of *p*-nitrophenol (from water, m.p. 111–113°) and 0.1 g. of 4,4'-dinitrobiphenyl. If the cuprous solution is added too rapidly the amount of biphenyl increases.

Decomposition of N-Nitroso-*p*-nitroacetanilide (NNA).—Solid NNA⁴³ (5 g., moist) was dissolved in 45 ml. of anhydrous acetone and the solution added to a mixture of 6 g. of ferric chloride hexahydrate, and 3 g. of lithium chloride in 75 ml. of acetone. After argon was bubbled through the solution briefly, it was heated (with the exclusion of air) in a water-bath at 60° for 24 hr. Water was added to the reaction mixture; the precipitate was filtered, dried and crystallized from petroleum ether. The yield of *p*-nitrochlorobenzene is 2.1 g. (84% based on nitrogen evolution). Insoluble unidentified material weighed 0.3 g.; the mother liquors yielded small amounts of nitrobenzene.

Decomposition of Phenylazotriphenylmethane.—An acetone solution (100 ml.) containing 5 g. (0.0142 mole) of phenylazotriphenylmethane⁴⁴ and 10 g. of ferric chloride hexahydrate was heated at 60° in a water-bath for 12 hr. The nitrogen evolution was complete in approximately 2 hr. From the reaction mixture 1.1 g. of chlorobenzene and 3.3 g. of triphenylcarbinol were isolated. The trityl chloride which was presumably formed in the reaction mixture was hydrolyzed either during the heating or subsequent work-up.

Meerwein Reaction. Decomposition of *p*-Nitrobenzenediazonium Chloride. (a) **Oxygen-free.**—Forty ml. (0.04 mole) of the diazonium solution mentioned previously was added to a solution of 200 ml. of acetone and 10 g. of acrylonitrile. A solution of cuprous chloride (0.5 g.) and lithium chloride (0.3 g.) in anhydrous acetone (30 ml.) was added dropwise to the deoxygenated solution at 0° with stirring. Nitrogen was evolved immediately. The solution on dilution with water yielded 8.1 g. of α -chloro-*p*-nitrohydrocinnamionitrile which was recrystallized from ligroin as colorless needles (94%, m.p. 110–111°).

Anal. Calcd. for $C_9H_7N_2O_2Cl$: C, 51.3; H, 3.36; Cl, 16.9. Found⁴⁵: C, 51.5; H, 3.48; Cl, 16.4.

(b) **With Iodine.**—An acetone solution of 16 g. of iodine was added to a deoxygenated solution containing 125 ml. of stock diazonium solution, 20 g. of acrylonitrile and 500 ml. of acetone at 0°. This was followed rapidly by an acetone solution of cuprous chloride (3 g.) and lithium chloride (2.5 g.). Nitrogen was evolved immediately and a heavy precipitate formed. The solution was diluted with water and filtered. The dried (30.3 g.) solid was triturated with small portions of ether. Evaporation of the ether left 6.6 g. of a solid from which no *p*-nitrochlorobenzene could be extracted with petroleum ether (b.p. 60–70°). It consisted wholly of a mixture of α -iodo and α -chloro-*p*-nitrohydrocinnamionitrile. These related compounds could not be separated. Neither careful fractional crystallization from ligroin or benzene nor partial vacuum sublimation were successful. In every case fine colorless needles (m.p. 103–104°, mix m.p. 107–109°) were obtained which on mild treatment with triethylamine in ligroin gave *p*-nitrocinnamionitrile (m.p. 198–201°). Iodide ion was present in the aqueous extracts of the ligroin solution. The infrared spectra (in CCl_4 and CS_2) were identical with those of the chloronitrile. The elemental analysis, calculated on the assumption that the iodocinnamionitrile was the sole contaminant, indicated that 13% of the mixture consisted of this unremovable impurity.

Anal. Calcd. for 13% iodo compound: C, 49.4; H, 3.22; total halide, 20.2. Found: C, 49.7, 5.00; H, 3.12, 2.99; total halide, 20.4, 20.3.

Decompositions of Diazonium Bisulfates (Minimum Chloride).

(43) R. Huisgen and G. Horold, *Ann.*, **562**, 137 (1919).

(44) R. Huisgen and H. Nakaten, *ibid.*, **586**, 70 (1954).

(45) Microanalyses by Drs. G. Weiler and F. Strauss, Oxford, England.

(a) **Oxygen-free.**—To a deoxygenated solution of 12 g. of NBDB in 50 ml. of water, 9 g. of styrene and 300 ml. of acetone was added dropwise a solution of cuprous chloride (7 g.) and lithium chloride in acetone at -20° . The nitrogen evolution occurred immediately and only on the continued cuprous chloride addition. The solution was decanted from the cupric sulfate precipitate, vacuum distilled and extracted with ether. Basic extractions of the ethereal solution were colored dark red. Acidification of the aqueous extract followed by ether partition gave only a small amount (0.1 g.) of material which was not *p*-nitrophenol. The original ether solution after drying (sodium sulfate) yielded 8.4 g. of a semi-crystalline material, which on alumina chromatography with petroleum ether and benzene yielded 1.5 g. of *p*-nitrochlorobenzene, 2.1 g. (16.5%) of α -chloro-*p*'-nitrobiphenyl (m.p. 91–92°), 0.98 g. (9%) of *p*-nitrostilbene (m.p. 154–156°) and 0.1 g. of 4,4'-dinitrobiphenyl (m.p. 230–234°).

Anal. Calcd. for $C_{14}H_{12}NO_2Cl$: C, 64.2; H, 4.62; N, 5.35. Found: C, 64.8; H, 4.70; N, 5.38.

The addition of 14 g. of cupric chloride to a similar reaction yielded 3.4 g. (27%) of the chlorobiphenyl compound and 0.35 g. of *p*-nitrostilbene. On the other hand, the addition of 26 g. of cupric nitrate trihydrate increased the proportion of *p*-nitrostilbene (2.3 g., 21%) to α -chloro-*p*'-nitrobiphenyl (0.17 g.). The reaction was accompanied by larger amounts of colored material not eluted with chloroform.

(b) **With Oxygen.**—A solution of styrene (9 g.) and 400 ml. of acetone containing 12.7 g. of crystalline NBDB and 40 ml. of water was chilled to -25° . Oxygen was bubbled vigorously through the solution with a fritted glass tube and maintained at 4 p.s.i. A solution of 7 g. of cuprous chloride and 5 g. of lithium chloride in 150 ml. of anhydrous acetone was added dropwise with stirring. The solution was decanted after the reaction was complete and vacuum distilled without warming above room temperature. The residue was extracted with chloroform, the light yellow chloroform solution was dried and vacuum distilled leaving a semi-solid mass (9.4 g.). This mixture was repeatedly extracted with petroleum ether at room temperature to remove the *p*-nitrochlorobenzene (19 g.) and a small amount of unidentified aldehydic material (not benzaldehyde). The residue from the petroleum ether extraction was crystallized from ethanol (1.6 g., 13%). It was identified as *p*-nitrodesoxybenzoin (m.p. 142–144°),⁴⁶ 2,4-dinitrophenylhydrazine,⁴⁷ m.p. 234–235°, oxime,⁴⁸ m.p. 104–105°. In addition, less significant amounts of *p*-nitrochlorobenzene (0.2 g.), *p*-nitrostilbene (0.05 g.) and 4,4'-dinitrobiphenyl (0.02 g.) were obtained. No *p*-nitrophenol was found.

Decomposition of N-Nitroso-*p*-nitroacetanilide.—Styrene (2.2 g.) was added to an acetone (120 ml.) solution of ferric chloride (6 g.), lithium chloride (3 g.) and NNA (5 g., moist) and heated at 60° for 12 hr. After the completion of the nitrogen evolution, water was added to the reaction mixture and the aqueous solution decanted from the brown oil. The styrene was allowed to evaporate and the semi-crystalline residue was chromatographed directly with ligroin and benzene mixtures. The yield of α -chloro-*p*'-nitrobiphenyl is 1.8 g. (43%); *p*-nitrochlorobenzene is 0.6 g. If present, *p*-nitrostilbene was not detected. Weight of tar is 0.6 g.

When 2.0 g. of acrylonitrile was added to the reaction as indicated above, 0.85 g. of *p*-nitrochlorobenzene, 0.51 g. (15%) of α -chloro-*p*-nitrohydrocinnamionitrile and 1.4 g. of tar was obtained. That acrylonitrile was incorporated in the tar is indicated by a nitrile absorption (2250 cm^{-1}) in the infrared spectrum. These results are in qualitative accord with the observations of the relative efficiency of ferric ion in terminating growing styryl and acrylonitrile radicals.³

The decomposition of NNA in the presence of metal ions is complicated by side reactions involving denitrosation.⁴³ Cuprous chloride denitrosates quantitatively in cold acetone solutions, whereas cupric chloride and chromic chloride do so only upon heating (probably due first to the reduction of the metal ion by acetone).²⁹ In the case of ferric chloride, *p*-nitroacetanilide formation is at its maximum when solu-

(46) P. Petrenko-Kritschenko, *Ber.*, **25**, 2242 (1892).

(47) E. Womack, N. Campbell and G. Dodds, *J. Chem. Soc.*, 1402 (1938).

(48) O. List, *Ber.*, **26**, 2453 (1893).

tions in acetone are saturated with lithium chloride (*i.e.*, in a highly complexed form). Ferrous chloride does not cause the formation of nitrous oxide; the products of this reaction consist of nitrobenzene and tar and are the same as those in the absence of metal ions. Decompositions of NNA in anhydrous dimethylformamide containing metal salts are complicated by reaction with solvent.⁴⁹

Decomposition of Phenylazotriphenylmethane.—Argon was flushed through an acetone solution (100 ml.) containing 5 g. (0.0143 mole) of PATM, 10 g. of ferric chloride and 15 g. of styrene. As the solution was heated at 60° in the absence of air, colorless needles of ferrous chloride were deposited on the sides of the flask. The solution was decanted, diluted with water and extracted with ether. The light yellow solution after washing with dilute sulfuric acid and water was dried and vacuum distilled. The semi-solid residue was extracted repeatedly with petroleum ether; the petroleum ether solution yielded on chromatography 1.7 g. of an oil. The oil easily solvolyzed in 50% aqueous acetone to give chloride and phenylbenzylcarbinol (m.p. 60–62°). Another portion of the oil was treated with alcoholic potassium hydroxide to yield stilbene (m.p. 123–125°). Authentic α -chlorobibenzyl made *via* the carbinol was the same as the oil. This compound eliminates hydrogen chloride spontaneously on standing.⁵⁰ The yield of chloride was based on the stilbene (46%) formed by basic treatment. The petroleum ether insoluble material was nearly pure triphenylcarbinol (3.4 g., 91%, m.p. 160–162°).

Benzoyl Peroxide Decomposition.—A mixture of 25 g. (0.206 equivalent) of benzoyl peroxide, 90 g. of ferric chloride hexahydrate, 20 g. of lithium chloride and 50 g. of styrene in 800 ml. of acetone was heated at 60° for 36 hr. in the absence of air. The carbon dioxide liberated was precipitated as barium carbonate (8.1 g., 0.041 mole). The acetone was vacuum distilled at room temperature and the residue was poured into dilute sulfuric acid and then extracted with ether. The ether extract was washed several times with 5% sodium bicarbonate (13.2 g. of benzoic acid, 0.108 mole). The ethereal solution after drying was distilled; it left an oily light residue (27 g.). The oil on fractionation *in vacuo* (0.35 mm.) gave: (a) 4.5 g., boiling 50–65°, mostly styrene; (b) 125–132°, 4.5 g.; (c) 160–165°, 13.5 g.; and (d) high boiling material, 2.1 g. Fraction b partially crystallized into a mixture of stilbene (2.7 g., 0.015 mole) and α -chlorobibenzyl (1.5 g., 0.007 mole) which were separated by solubility in petroleum ether (b.p. 30–40°). Fraction c on redistillation consisted almost wholly of a compound boiling at 164–165° at 0.7 mm. This chlorine-containing compound solvolyzed readily in aqueous acetone; basic hydrolysis of the resulting oil in dioxane–water solutions yielded benzoic acid and water-soluble styrenediol (m.p. 64–64°).⁵⁰ The compound probably has the structure $C_6H_5CO_2CH_2CHClC_6H_5$.

Anal. Calcd. for $C_{13}H_{13}O_2Cl$: C, 69.0; H, 5.02; Cl, 13.6. Found: C, 69.5, 69.7; H, 4.99, 5.10; Cl, 13.3.

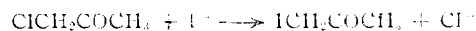
The yields depend to a large extent on the ratio of ferric chloride to added lithium chloride. With no added lithium chloride the decomposition in the presence of styrene leads to

(49) P. Onyon, *Trans. Faraday Soc.*, **52**, 80 (1956).

(50) N. Milas and S. Sussman, *This Journal*, **59**, 2345 (1937).

more high boiling residue than those reactions with added chloride. Neither stilbene nor chlorobibenzyl could be isolated from the former solutions. It has not been determined yet whether the ester arises *via* a ferric-catalyzed homolytic or heterolytic⁵¹ process. This reaction merits further investigation.

Decomposition of Diazonium Salts in the Presence of $CuCl_2$.—Standard stock solutions were made from crystalline diazonium chlorides, reagent cupric chloride and lithium chloride as described previously.² Freshly crystallized cuprous chloride was dissolved in anhydrous acetone (0.064 *M*) with the aid of lithium chloride and aliquots were sealed in 1-, 2- and 3-ml. thin walled ampules. The aqueous cupric chloride solution was placed in the center well of the reaction vessel; the diazonium salt, lithium chloride and vial of cuprous chloride solution together with acetone were placed in the outer well. The vessel was degassed by the standard procedure. The evacuated flask was then shaken at 0° to break the ampule containing cuprous chloride. After the reaction was complete (test with β -naphthol solution), acidic ferric ammonium sulfate solution was added and the solution vacuum distilled into a Dry Ice trap. Under these conditions acetone, chloroacetone and water were collected. To the thawed solution was added 4 g. of sodium iodide and the volume made up to 50 ml. with acetone. The iodoacetone was analyzed by acidifying an aliquot with aqueous perchloric acid and quickly titrating with standard sodium thiosulfate solution. Control runs proved to be accurate within 3%. The stoichiometry of the reactions are⁵²



The residual ferrous ion was titrated with standard ceric solution. The extent of oxidation of the ferrous salt during the distillation is negligible.

TABLE III

EFFECT OF IODINE ON CHLOROACETONE FORMATION^a

Cuprous chloride, meq.	Iodine, mg.	Chloroacetone, ^b meq.
0.128	..	1.02
.128	300	0.47
.128 ^c	300	.17
.128 ^d	300	.0
.256	..	1.75
.256	300	0.63
.256	600	.50
.256	900	.46

^a Same as Table I for *p*-chlorobenzenediazonium chloride.

^b Includes iodoacetone formed from iodine. ^c No cuprous salt. ^d No diazonium salt.

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(51) J. Leffler, *ibid.*, **72**, 67 (1959). D. Bryce Smith and P. Clarke, *J. Chem. Soc.*, 2264 (1956).

(52) J. Conant and W. Kirder, *This Journal*, **46**, 233 (1925).