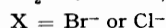
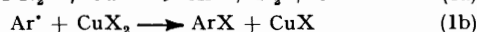
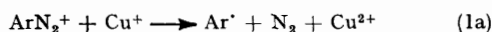


Evidence for the Intermediacy of the Aryl Radical in the Sandmeyer Reaction

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The competition between bromodiazotiation and chlorodiazotiation is exploited as a test of the occurrence of an aryl radical in the Sandmeyer reaction pathway. The use of five reducing agents, covering a wide range of redox ability, is shown not to influence the experimental $k_{\text{Br}}/k_{\text{Cl}}$ values. The intermediacy of a common species is consequently inferred and supported by independent generation of the phenyl radical by decomposition of benzoyl peroxide. Considerations on the rates of the ligand transfer processes are put forward.

FROM the beginning of its use in preparative chemistry the mechanism of the Sandmeyer reaction has aroused interest. The radical nature of the process was first recognized by Waters.¹ Kochi later proposed² a reaction scheme comprising the transfer of an electron by the Cu^+ ion (1a) and a ligand transfer step (1b). Consis-



SCHEME

tent with this Scheme, it has been recently shown³ that the presence of both a reducing species and a ligand transfer agent is required. The reductant role can be fulfilled by species † other than Cu^+ , the only requisite being a redox potential equal or less than 1 V.³ For the sake of efficiency, the preferred ligand transfer agent is the Cu^{2+} ion, which includes added halide ion in its coordination sphere and which then transfers the halogen atom in step (1b).³⁻⁶

However, no clearcut evidence has so far been produced as to the nature of the product of the reduction step (1a). After Kochi the intermediacy of a free aryl radical has been generally assumed, but the earlier Cowdrey-Davies proposal⁷ of a 'crypto radical' has never been firmly disproved, that is that the substrate diazonium salt is associated to the copper(I) ion.

In order to gain insight into this problem, advantage was taken of the ability of several reductants (M^{n+}) to promote the Sandmeyer reaction.³ If the reaction intermediate is a truly free aryl radical and if the mechanism is correctly represented in the Scheme, competitive halogenodiazotiation reactions of known amounts of Br^- and Cl^- in the presence of the ligand transfer agent Cu^{2+} should give the same $\text{ArBr}:\text{ArCl}$ product ratio independent of the reductant employed for step (1a).

This expectation is fulfilled by the results reported below. Moreover, this approach has allowed us to draw some considerations on the fundamental problem of the rate of the ligand transfer step.

† For other reducing agents besides those reported in ref. 3 see A. Citterio, F. Minisci, A. Albinati, and S. Bruckner, *Tetrahedron Lett.*, 1980, 2909.

RESULTS AND DISCUSSION

The reductants examined in this study (SnCl_2 , CuCl , ferrocene, FeSO_4 , and ascorbic acid) cover a wide range of appropriate E_0 values (respectively 0.15, 0.16, 0.31, 0.77, and 0.86 V)⁸ and were supplied in stoichiometric amounts with respect to the substrate. The ligand transfer agent was $\text{Cu}(\text{NO}_3)_2$ in all cases. The reactions were run on arenediazonium nitrates at room temperature in H_2O -dioxan (2:1, v/v) to ensure complete solubility of both the inorganic and the organic reagents.

To minimize any counterion effects proceeding from preferential interaction between the reductant and one of the halide ions, a 'buffer' concentration of Br^- and Cl^- was always supplied. Variation from a three- to an eight-fold excess of Br^- and Cl^- with respect to the diazonium salt did not appreciably affect the results (see Table I). Moreover, in all the experiments two equivalents of ligand transfer agent per equivalent of substrate were employed to overcome possible interactions between the Cu^{2+} salt and the reductant, which might affect the competitive results.

The results are shown in Table 1. Benzenediazonium salt was subjected to wider investigation with several reductants and will be examined first. It is noteworthy that bromine is always transferred with greater ease than chlorine by the Cu^{2+} ion. This was observed earlier^{3,5,9} and may be regarded as further proof that the same kind of mechanism operates with all the reductants. A second and most prominent peculiarity appears from the $k_{\text{Br}}:k_{\text{Cl}}$ ratios. These values are the same within experimental uncertainty and do not depend on the reductant employed. This constancy suggests that the ligand transfer agent always interacts with the same intermediate, regardless of which reducing agent produced it. The same is true in the case of the other substrates, where the investigation was limited to the best and to the worst reductant within the series.

Were the reductant associated with the substrate to form the reaction intermediate, a variety of such species would be expected. The selectivity of bromine and chlorine transfer to these intermediates would likely be affected by the different steric and electronic requirements of the intermediate itself, resulting in different

reactivity ratios. In particular, the presence in the substrate of a substituent in the *ortho*-position or that of the bulky α -naphthyl group could be expected to play a significant role and to make the situation different from intermediate to intermediate. No such effect was found.

alkyl radicals.* It is reassuring to observe that the rates of bromine and chlorine transfer were determined by Kochi and Jenkins in competitive kinetics studies based on the isomerization of both hex-5-enyl radical and cyclopropyl radical.^{10b} These experiments provided results which are indistinguishable from one another, yet

TABLE 1

Competitive halogenodediazoniatio reactions on arenediazonium nitrates under stimulation by several reducing agents in water-dioxan (2 : 1) at room temperature

Substrate	Stimulant M ⁿ⁺	Reaction time (min)	Products (%) ^a		k_{Br}/k_{Cl} ^b
			ArBr	ArCl	
C ₆ H ₅ N ₂ ⁺	Sn ²⁺	5	57	19	3.0 ± 0.2
	Sn ²⁺	5	55	19	2.9 ± 0.1 ^c
	Sn ²⁺	5	58	18	3.2 ± 0.1 ^d
	Cu ⁺	5	56	19	2.9 ± 0.1
	Fc ^e	5	45	15	3.0 ± 0.2
	Fe ²⁺	5	35	12	2.9 ± 0.2
	Ascorbic acid	5	28	9	3.1 ± 0.1
	Ascorbic acid	10	51	17	3.0 ± 0.2
	Ascorbic acid	10	5	1.6	3.2 ± 0.1
<i>p</i> -CH ₃ OC ₆ H ₄ N ₂ ⁺	Sn ²⁺	10	3	1.0	3.1 ± 0.1
	Ascorbic acid	10	3	1.0	3.1 ± 0.1
<i>o</i> -ClC ₆ H ₄ N ₂ ⁺	Sn ²⁺	10	34	9	3.8 ± 0.2
	Ascorbic acid	10	30	8	3.7 ± 0.1
α -NaphthylN ₂ ⁺	Sn ²⁺	10	8	1.4	5.6 ± 0.2
	Ascorbic acid	10	6	1.1	5.4 ± 0.2
<i>p</i> -O ₂ NC ₆ H ₄ N ₂ ⁺	Sn ²⁺	5	54	25	2.1 ± 0.1
	Ascorbic acid	5	46	23	2.0 ± 0.1
C ₆ H ₅ N ₂ ⁺	Sn ²⁺	10	2	4	0.46 ± 0.02 ^f

^a Determined by g.l.c. analysis. ^b Reckoned according to the equation reported in the Experimental section. The amount of both Br⁻ and Cl⁻ was *ca.* 5 times the molar amount of substrate. The ligand transfer agent was Cu(NO₃)₂ unless otherwise indicated. ^c The amount of both Br⁻ and Cl⁻ was *ca.* 3 times that of the substrate. ^d The amount of both Br⁻ and Cl⁻ was *ca.* 8 times that of the substrate. ^e Ferrocene. ^f Employing Fe(NO₃)₃ as the ligand transfer agent.

Hence it is reasonable to conclude that in the Sandmeyer reaction a free aryl radical is the intermediate, generated by the reduction of the arenediazonium salt.

It is of interest to compare the range of the competitive $k_{Br} : k_{Cl}$ results for arenediazonium salts with the rates of halogen transfer from CuX₂ to alkyl radicals measured

there is a variation in the rates of isomerization of the two reference compounds of a factor of 10³.

Hence it may be suggested that the $k_{Br} : k_{Cl}$ ratios reported in Table 1 reflect the different ease of halogen transfer from Cu²⁺ ion to aryl radical. The importance of the mediation of the cation in this process is stressed by

TABLE 2

Competitive halogen-transfer in the decomposition of benzoyl peroxide^a

Other reagents	T/°C	Products (%) ^b					$k_{Br} : k_{Cl}$
		PhBr	PhCl	PhH	Ph ₂	PhOH	
Cu(NO ₃) ₂ , Br ⁻ , Cl ⁻	100 ^c	3.6	0.69	47	0.4	9	5.2 ± 0.2
Br ⁻ , Cl ⁻	100 ^c	0.61	0.02—0.06	60	1	1	Not determined
Cu ⁺ , Cu(NO ₃) ₂ , Br ⁻ , Cl ⁻	55 ^d	12	2.4	39	0.2	4	4.7 ± 0.2

^a The yields were determined by g.l.c. analysis. Reaction time 3 h. The amount of the other reagents was as indicated in Table 1. ^b Yields were evaluated relative to the peroxide. Minor traces of other products were also observed but not further identified. ^c In water-dioxan (2 : 1). ^d In AcOH-water (5 : 1), catalysed by Cu⁺ salt.

by Kochi and Jenkins.¹⁰ They determined a rate of 4.3×10^9 for bromine and 1.1×10^9 l mol⁻¹ s⁻¹ for chlorine, giving a ratio (3.9) remarkably close to the $k_{Br} : k_{Cl}$ competitive values collected in Table 1. It is difficult to say whether this closeness is significant or just fortuitous in view of the scant data available on related reactivity ratios. It should be noted, however, that the rates of halogen transfer reported by Kochi and Jenkins approach the diffusion-controlled limit. As preliminary results indicate,¹¹ this should hold in the case of aryl radicals as well. Hence, if these ligand transfer processes are so fast, it is no wonder that the copper(II) salt is not able to appreciably discriminate between aryl and

the experiment with Fe³⁺ as the ligand transfer agent (Table 1) and shows a markedly different $k_{Br} : k_{Cl}$ ratio.

An independent piece of evidence was sought in support of the intermediacy of aryl radicals. Benzoyl peroxide is known to yield phenyl radicals by thermal

* When atom abstraction processes, and not atom transfer *via* a copper(II) salt, are concerned wider differences in the $k_{Br} : k_{Cl}$ ratio can be observed, as reported by Giese and Keller¹² for some primary alkyl radicals ($k_{Br} : k_{Cl}$ 1 500—4 500 in the range 50—0 °C) and by Lorand *et al.*¹³ for phenyl radical ($k_{Br} : k_{Cl}$ 1 500 at 45 °C; k_{Br} 5.0×10^9 and k_{Cl} 3.5×10^6 l mol⁻¹ s⁻¹). The rate of the latter process relative to chlorine is now well below the encounter-controlled region. Nevertheless, even in this case the halogen reactivity ratios for alkyl and aryl radicals do not differ much.

decomposition,¹⁴ and reacted in the presence of CuBr₂ and CuCl₂ in water-dioxan (2 : 1, v/v) at 100 °C. After 3 h, bromo- and chloro-benzene were found among the products (Table 2). A blank experiment in the presence of Br⁻ and Cl⁻ but without any added Cu²⁺ salt revealed only trace amounts of halogenobenzenes, which again stresses the need for copper(II) ion as ligand transfer agent.

Since the halogenodiazonation reaction and the thermal decomposition of benzoyl peroxide require rather different experimental temperatures, a Cu^I-catalysed decomposition of the peroxide,^{6,15} which occurs easily at only 55 °C, was also performed for a closer comparison. Under both decomposition conditions the major product is benzene, as is usually found.¹⁶

If allowance is made for the different reaction environment, temperature, and method of generation of the aryl radical, the $k_{\text{Br}} : k_{\text{Cl}}$ ratios determined for the decompositions of benzoyl peroxide (Table 2) appear to be in remarkably close agreement with those reported in Table 1. This finding, arising from an independent experimental approach of phenyl radical generation, strengthens the conclusion that an aryl radical is indeed the intermediate in the Sandmeyer halogenodiazonation reaction.

EXPERIMENTAL

Reagent-grade commercially available compounds were used throughout.

Arenediazonium nitrates were prepared as described elsewhere.³ Then, while kept at *ca.* 5 °C, the proper amounts of NaBr and LiCl were added. When they were dissolved, the Cu(NO₃)₂ salt (2 equiv.) was added. Finally, the ice-water bath was removed and a concentrated solution of the reductant (1 equiv.) was added in one go. The resulting mixture was stirred at room temperature for 5 or 10 min, quickly quenched by dilution with water and extraction with ether after the addition of the internal standard, washed with water, and dried (Na₂SO₄).

The benzoyl peroxide decomposition experiments were run under nitrogen.⁹ When CuCl was used to induce peroxide decomposition, it was added to a solution of the other reagents kept at 55 °C. A work-up of the mixture similar to that of the diazonium experiments was adopted.

Product yields were determined by g.l.c. analysis performed on a Hewlett-Packard 5830A flame ionization in-

strument fitted with a 100 cm × 4 mm column of 3% OV-17 on 80–100 mesh Chromosorb GAW-DMCS. Molar response factors with respect to the internal standard were determined and used in the evaluation of g.l.c. results. Relative reactivity was calculated by equation (2)¹⁷ where [Br⁻]₀

$$\frac{k_{\text{Br}}}{k_{\text{Cl}}} = \frac{\ln[\text{Br}^-]_0/[\text{Br}^-]_t - [\text{ArBr}]_t}{\ln[\text{Cl}^-]_0/[\text{Cl}^-]_t - [\text{ArCl}]_t} \quad (2)$$

and [Cl⁻]₀ are initial concentrations and [ArBr]_t and [ArCl]_t are concentrations of products at time *t*. The amount of halide ion, whenever it was introduced as the counterion of the stimulant, was taken into account in reckoning the $k_{\text{Br}} : k_{\text{Cl}}$ reactivity ratios according to equation (2).

A control experiment of competitive halogenodiazonation in AcOH-water (5 : 1, v/v) was also run on benzenediazonium nitrate under SnCl₂ stimulation. It afforded a result equal to those reported in Table 1.

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