

Reactivity and Stability of Arenediazonium Ions

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The reactions of arenediazonium ions are among the oldest to be studied intensively by organic chemists. The discussion between A. Hantzsch and E. Bamberger in the period 1894–1912 concerning the structure of the products formed in the reactions of arenediazonium ions with hydroxide, cyanide, and sulfite ions is well known. It was probably one of the first times in which arguments based on the ideas of physical organic chemistry, in this case presented by Hantzsch, prevailed over the views held by a classical organic chemist.

In the early days of physical organic chemistry proper, Robinson, Conant, and Bartlett¹ realized that diazo coupling reactions belong to the large class of electrophilic aromatic substitution reactions. Indeed, it was shown later² that these coupling reactions are extraordinarily well suited to the investigation of the preequilibria as well as the substitution proper.

The observation³ that arenediazonium ions are dibasic (Lewis) acids with the astonishing characteristic that, in contrast to all dibasic Brønsted acids, their first acidity constant is *smaller* than the second ($K_1 < K_2$) is an important prerequisite for the understanding of the homolytic decomposition of diazonium ions in the Gomberg–Bachmann reaction. The mechanism of this reaction was elucidated by Rüchardt, *et al.*;⁴ it is closely related to the decomposition of acylarylnitrosamines.⁵

The diazonium group is also an interesting substituent inasmuch as it is by far the most strongly electron-attracting substituent known ($\sigma_p = 1.8$).⁶

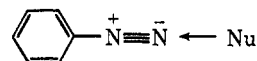
The purpose of this Account is to give a critical review of present knowledge concerning some types of reactions of arenediazonium ions that, in the opinion of the author, may become particularly interesting in the near future. These are as follows: (i) the relationship between *cis* and *trans* additions of nucleophiles to the β nitrogen of diazonium ions in light of the fact that diazonium ions belong to that unique group of cations whose reactions with nucleophiles are not disguised by reorganization effects of the solvent surrounding the cation;⁷ (ii) the question of whether aryl cations are really intermediates formed from di-

azonium ions in heterolytic dediazoniations;⁸ (iii) the gradual changeover from heterolytic to homolytic dediazoniations, the problem of a common intermediate for these two types of reactions,⁹ and potential correlations of this problem with the observed¹⁰ N_α – N_β inversion in diazonium ions and with metal complexes which are able to react with molecular nitrogen;¹¹ (iv) the stability of arenediazonium salts. This topic is important from both the scientific and the safety point of view. In 1969, for example, the unexpected decomposition of 1200 mol of 2,4-dinitro-6-chlorobenzenediazonium bisulfate in concentrated sulfuric acid caused the death of three workmen. It is through the joint efforts of analytical, physical, and physical organic chemists that the causes of such explosions can be elucidated and precautions taken to prevent industrial accidents.

A Classification of Reactions of Arenediazonium Salts

Reactions of arenediazonium ions can be classified into seven types.

I. Reactions with Nucleophiles (Nu) at the β Nitrogen. Nucleophiles may be anions ($-\text{OH}$, $-\text{OR}$, $-\text{OAr}$, $-\text{CN}$, $-\text{N}_3$), ammonia, amines and, in diazo coupling reactions, π -electron systems containing electron-donating substituents.



(1) R. Wistar and P. D. Bartlett, *J. Amer. Chem. Soc.*, **63**, 413 (1941), and references cited therein.

(2) H. Zollinger, *Chem. Rev.*, **51**, 347 (1952); *Helv. Chim. Acta*, **36**, 1070, 1723, 1730, 1732 (1953); **38**, 1597, 1617, 1623 (1955); C. Wittwer and H. Zollinger, *ibid.*, **35**, 1209 (1952).

(3) C. Wittwer and H. Zollinger, *Helv. Chim. Acta*, **37**, 1954 (1954).

(4) C. Rüchardt, B. Freudenberg, and E. Merz, *Chem. Soc., Spec. Publ.*, **19**, 154 (1965).

(5) J. I. G. Cadogan, *Chem. Soc., Spec. Publ.*, **24**, 71 (1970); *Accounts Chem. Res.*, **4**, 186 (1971).

(6) E. S. Lewis and M. D. Johnson, *J. Amer. Chem. Soc.*, **81**, 2070 (1959).

(7) C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972), and references cited therein.

(8) The nomenclature used in this article follows the systematic nomenclature for substitution reactions proposed by J. F. Bunnett, *J. Chem. Soc.*, 4717 (1954): first the name of the group (or atom) introduced is given, followed by *de-* and the name of the leaving group. *E.g.*, ordinary nitration is called nitrodeprotonation; the hydrolysis of picryl chloride is hydroxydechlorination, etc. Reactions of arenediazonium ions in which N_2 is the leaving group are dediazoniations, *e.g.*, hydroxydediazonation, protodediazonation. For leaving groups, we differentiate electrofugal (*e.g.*, H^+ , CO_2^-) and nucleofugal groups (*e.g.*, Cl^- , N_2^+).

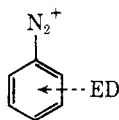
(9) T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970).

(10) J. M. Insole and E. S. Lewis, *J. Amer. Chem. Soc.*, **85**, 122 (1963); E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32, 34 (1964); E. S. Lewis and R. E. Holliday, *ibid.*, **88**, 5043 (1966); **91**, 426 (1969); E. S. Lewis and P. G. Kotcher, *Tetrahedron*, **25**, 4873 (1969).

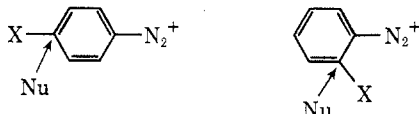
(11) Reviews: (a) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **8**, 650, (1969); (b) M. E. Vol'pin, *Pure Appl. Chem.*, **30**, 607 (1972); (c) W. Preetz, *Angew. Chem., Int. Ed. Engl.*, **11**, 243 (1972).

Heinrich Zollinger received his B.Sc. (in 1943) and Ph.D. (in 1944) from the Swiss Federal Institute of Technology ETH, Zurich. He then joined the Dyestuff Research Department of the CIBA Company in Basle, Switzerland, and after research leave at M.I.T. (1951–1952) became a lecturer at Basle University. In 1960 he returned to the ETH in Zurich where he became Professor of Dyestuff and Textile Chemistry. In 1973 he was elected Rektor of ETH, *i.e.*, Academic President. His research interests include studies of aromatic and heteroaromatic substitutions, reactions of arenediazonium ions, the reactions of formaldehyde with amines, urea, and cellulose, methods for the elucidation of the chemical structure of cellulose derivatives, dye sorption mechanisms on fibrous polymers, and diffusion-controlled processes in homogeneous and heterogeneous systems.

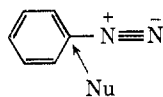
II. Formation of Complexes with Electron Donors (ED). Complex formation¹² is greatly facilitated by the electron-attracting effect of the diazonium group.⁶



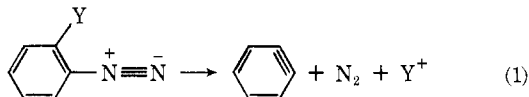
III. Substitution of Nucleofugal Leaving Groups (X) in the Ortho or Para Position of the Aryl Nucleus. A well-known¹³ but little investigated example is the substitution of nitro by hydroxyl groups in solutions of the 2,4-dinitrobenzenediazonium ion. The reaction probably follows the S_NAr mechanism¹⁴ of nucleophilic aromatic substitution.



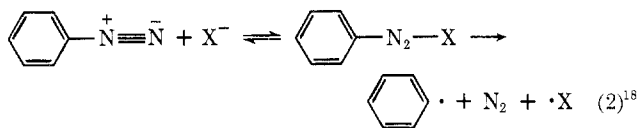
IV. Heterolytic Dediazoniations with Nucleophiles. The well-known hydroxydediazoniations and related reactions are discussed in this paper.



V. Formation of Arynes by Loss of N₂ and an Ortho Substituent. The electrofugal leaving group Y may be a proton^{15,16} or carboxylate.¹⁷



VI. Homolytic Cleavage of the C(1)-N_α Bond. Classical examples are the Gomberg-Bachmann reaction and protodediazoniations. In this Account attention is given to the role of so-called nucleofugal leaving groups (see below) formed by reaction type I (see above) with a nucleophile X⁻ (or X) which may form a relatively stable radical when leaving the intermediate (eq 2).



VII. Photolytic Dediazoniations. Hydroxy-, alkoxy-, and protodediazoniations are known and de-

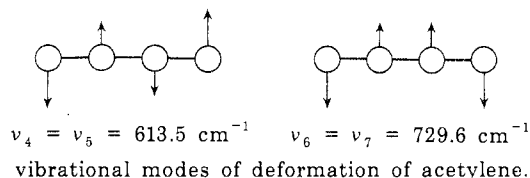
pend on the reaction conditions and substituents, but they are not discussed in this paper.

Reactions with Nucleophiles at the β Nitrogen

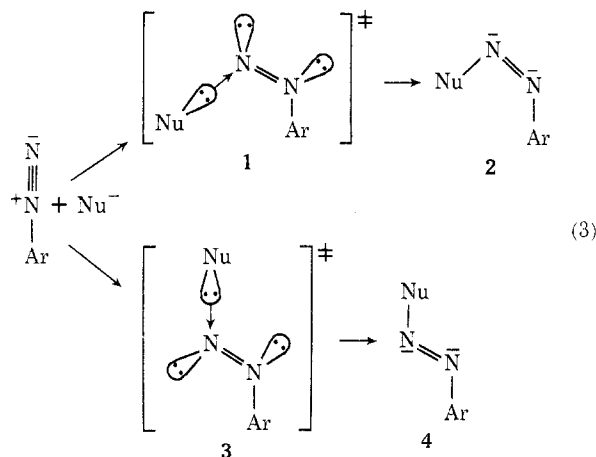
In the reactions of nucleophiles with diazonium ions, the rate-determined product is, in many cases, a cis azo compound in spite of the fact that the trans isomers are thermodynamically more stable. In general, the formation of trans azo compounds is observed only when the cis isomer is so unstable that it is not detected at all, except by a photochemical rearrangement.

At first sight, this experimental result is astonishing as the diazonium ion has, at least in crystals¹⁹ and probably also in solution, a linear axis C₁-N_α-N_β. To our knowledge, potential reasons for this observation have not yet been discussed.

In several respects the arenediazonium ions show analogies to acetylene. Acetylene has two deformation vibrations, ν₄ at 613.5 cm⁻¹ and ν₆ at 729.6 cm⁻¹.²⁰ The fact that the symmetric vibration ν₄ has a lower frequency than ν₆ can be understood from Bartell's²¹ valence-shell electron-pair repulsion (VSEPR) model on the basis of a "pseudo-Jahn-Teller" effect.²²



If a monoarylacetylene (ArC≡CH) is taken as a model for a transition state of an arenediazonium ion with a nucleophile Nu, two types of transition states, 1 and 3 in eq 3, can be visualized, 1 leading to the cis



azo compound 2 and 3 resulting in the trans isomer 4. If the transition state is reactant-like (i.e., "early"

(12) S. Koller and H. Zollinger, *Helv. Chim. Acta*, **53**, 78 (1970).

(13) H. Zollinger, "Diazo and Azo Chemistry," Interscience, New York, N. Y., 1961: (a) p 142; (b) p 165; (c) p 51; (d) p 175.

(14) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); C. F. Bernasconi, *Int. Rev. Sci. Org. Chem., Ser. 1*, **3**, 33 (1973).

(15) J. I. Cadogan and P. G. Hibbert, *Proc. Chem. Soc., London*, 338 (1964); D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. P. Harper, and J. T. Sharp, *J. Chem. Soc. B*, 1996 (1971); C. Ruchardt and C. C. Tan, *Angew. Chem., Int. Ed. Engl.*, **9**, 522 (1970); V. Hassmann, C. Ruchardt, and C. C. Tan, *Tetrahedron Lett.*, 3885 (1971).

(16) C. Ruchardt and C. C. Tan, *Chem. Ber.*, **103**, 1774 (1970).

(17) M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, **82**, 3802 (1960); R. Gompper, G. Seybold, and B. Schmolke, *Angew. Chem., Int. Ed. Engl.*, **7**, 389 (1968), and many other papers.

(18) X may be a molecule or an anion.

(19) C. Römning, *Acta Chem. Scand.*, **17**, 1444 (1963).

(20) T. Feldmann, G. G. Shepherd, and H. L. Welsh, *Can. J. Phys.*, **34**, 1425 (1956).

(21) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968). Note Added in Proof. In a recent discussion with the author Professor Bartell suggested that interaction between the lone pair at N_β and the aryl nucleus may be indirect, i.e., through a consecutive distortion of the C-N and N=N bonds.

(22) I thank Dr. H. B. Bürgi, ETHZ, for valuable suggestions on this problem.

on the reaction coordinate), repulsive interaction between the nucleophile and the aryl nucleus is small because the distance Nu-N_β is still large. Therefore, the repulsion between the lone pair at N_β and the aryl nucleus becomes decisive; it favors a trans configuration of the N_β lone pair with respect to the aryl nucleus (obviously it is energetically more dominant than the repulsion between the lone pairs at N_α and N_β); therefore, transition state 1 is on a lower energy level, and Nu attacks N_β in cis configuration.

If, however, the transition state is product-like ("late"), the Nu-N_β distance is short; repulsion between Nu and Ar is stronger than that between the N_β lone pair and Ar, and the transition state 3 leading to trans azo compound 4 is favored.

Can we check this model? Do we have evidence that reactions of arenediazonium ions and nucleophiles which have "early" and "late" transition states yield cis and trans azo compounds, respectively?

Cis compounds are formed in reactions with hydroxide, methoxide, cyanide, and sulfite ions; trans compounds are the products in reactions with amines (formation of triazenes or diazoamino compounds) and with diazo coupling components such as phenols and aromatic tertiary amines.

In investigations⁷ which are discussed from another point of view below, Ritchie and Wright²³ found ρ values between 2.3 and 2.6 for the rates of coordination of substituted benzenediazonium ions with hydroxide, cyanide, azide, and arylsulfonic acid anions, and ρ values between 3.5 and 5.2 for the respective equilibrium constants. The ρ values for the rates of two diazo coupling reactions are, however, 3.85 (reaction with 2-naphthol-6-sulfonic acid dianion) and 4.26 (2-naphthylamine-6-sulfonic acid dianion).²⁴ The ρ values of these rates are therefore significantly higher than those of reactions with other nucleophiles, but comparable to the ρ values of the equilibria mentioned. This indicates that the transition states of diazo coupling reactions are more product-like than for diazonium ion coordination with anions like OH^- , CN^- , and N_3^- . Moreover, attraction of the nucleophile to the π system of the aryl nucleus in 1 may favor cis attack, but only if Nu is a strong nucleophile such as OH^- .²⁵ This comparison supports therefore the explanation given above for cis vs. trans azo product formation. It is also consistent with general expectations: the coordination of a cation with a small anion which has a localized or almost localized negative charge is likely to have a more reactant-like transition state than the reaction of a cation with a molecule or an anion such as phenoxide ion whose negative charge is highly delocalized. Figure 1 represents schematically the reaction pathways for addition of nucleophiles to arenediazonium ions with "early" and "late" transition states.

The conclusion that the transition state of diazo coupling reactions is product-like (*i.e.*, similar to the σ -complex intermediate) is also welcome because the

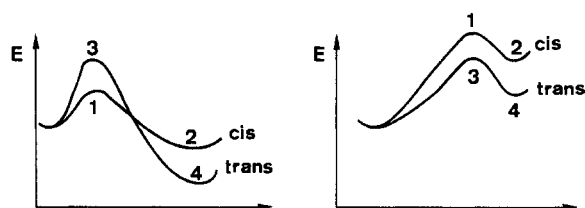


Figure 1. Potential energy along the reaction coordinate for reactions of β nitrogen of arenediazonium ions with nucleophiles yielding cis and trans azo compounds. (a, left) Reactant-like transition states (*e.g.*, reaction with OH^-); (b, right) Product-like transition states (*e.g.*, diazo coupling reaction with phenoxide ions; product = cyclohexadienone-type σ complex²⁶).

other methods for differentiating "early" and "late" transition states in electrophilic aromatic substitution²⁶ cannot be used for diazo coupling reactions.

Reactions of arenediazonium ions with nucleophiles became particularly interesting when Ritchie, *et al.*,⁷ found that three groups of cations, arenediazonium, triarylmethyl, and tropylium ions, although differing in reactivity by six powers of ten, give the unique reactivity sequence $\text{N}_3^- > \text{CH}_3\text{O}^-$ (or OH^-) $> \text{CN}^-$. This nucleophilicity order was observed in four solvents (H_2O , CH_3OH , dimethyl sulfoxide (DMSO), and dimethylformamide (DMF)). It is interpreted as being an inherent property of the nucleophiles and is related to the solvation energies of the nucleophiles. Ritchie concluded that the transition states of these cation-anion combination reactions are very close in structure to that of the one-solvent-separated ion pair, and that two factors are important in determining the relative rates of reaction with the four nucleophiles mentioned: (1) desolvation energy of the anion; (2) effective ionic radii of the cation and anion, which determine Coulombic attraction.

The investigation of reactions which do not involve the necessity for the displacement of a leaving group offers, thus, a convenient measure of nucleophilic reactivities. The situation concerning substitution reactions in which the nucleophile displaces a leaving group is not so well established, but it is clear that factors other than desolvation of the nucleophile are involved. Reactions such as diazo coupling in which the solvent and the charge and structure of the nucleophile can be varied may provide insight into some of these factors. The rate of the reaction between 4-toluenediazonium salts and *N,N*-dimethylaniline in sulfolane (tetramethylene sulfone), acetonitrile, water, and nitromethane varies only by a factor of 5.²⁷ Furthermore, no significant effect of the anion of the diazonium salt is found. It was inferred that the solvation of diazonium ions and the interaction in the ion pair are weak. However, a reinvestigation²⁸ of this reaction in acetonitrile and nitromethane shows that in these solvents it is a two-step process (SE2), the proton transfer being rate limiting. The measured rate constant may therefore be a complex combination of elementary rate constants. Nevertheless, the fact that charge-transfer formation of a

(23) C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, **93**, 2429, 6574 (1971).

(24) H. Zollinger, *Helv. Chim. Acta*, **36**, 1730 (1953).

(25) We thank Professor J. F. Bunnett for this suggestion.

(26) P. Rys, P. Skrabal, and H. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 874 (1972).

(27) J. R. Penton and H. Zollinger, *Helv. Chim. Acta*, **54**, 573 (1971).

(28) J. R. Penton and H. Zollinger, unpublished work.

diazonium salt decreases its reactivity only slightly,¹² in contrast to the situation found in sulfonation,²⁹ shows that the salt is poorly solvated.

Ritchie's work with diazonium ions and the other cations mentioned is clearly directed to the investigation of reactivities of nucleophiles. The further investigations mentioned above indicate, in our opinion, that diazonium ions are good candidates for the investigation of "intrinsic" electrophilic reactivity in solution, *i.e.*, of reactivity which is as little as possible disguised by solvation effects.

Nucleophilic Reactions at C-1

Nucleophilic dediazoniations of arenediazonium ions are generally considered the only cases of an SN1 mechanism in nucleophilic aromatic substitution and, therefore, the source of aryl cations.³⁰ As well as undergoing hydrolysis and substitution by halide ion, diazonium salts can act as arylating agents in heterolytic arylations of aromatic compounds. Conditions under which such reactions occur have been found recently by four groups.³¹⁻³⁴ These reactions might well be called "heterolytic Gomberg-Bachmann reactions."

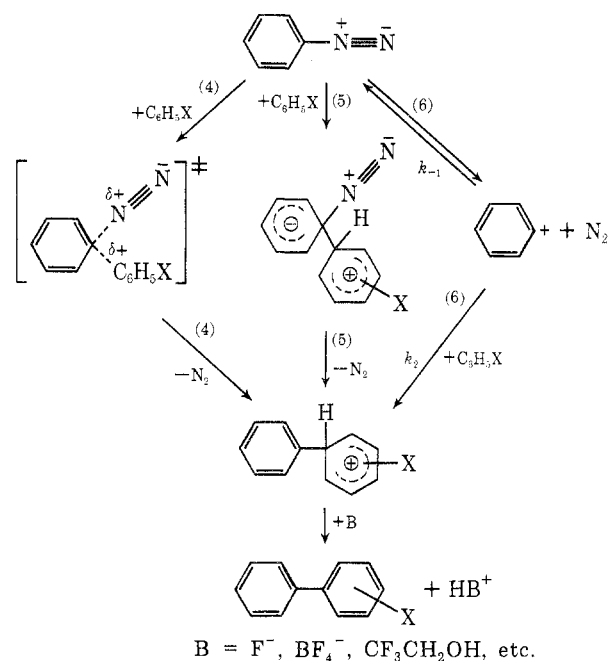
Experimental results are now discussed which are less consistent with an SN1 mechanism for such reactions than with a mechanism with a bimolecular rate-determining step.

Little attention has been given to a paper published in 1952 by Lewis and Hinds³⁵ who demonstrated that the decomposition rate of *p*-nitrobenzenediazonium ions in water is linearly proportional to added bromide ion. More recently, Lewis, *et al.*,³⁶ made a careful investigation of salt effects on the rate of decomposition of several arenediazonium ions in water. For several anions, linear dependences of the rates of decomposition on the concentration of the anion were found; this suggests participation of the nucleophile in the rate-determining step. The low selectivity of this reaction between nucleophiles,³⁷ however, makes this demonstration inherently difficult; possibly, the results are confused by medium effects.

A straightforward kinetic demonstration of nucleophilic participation was found in arylations of toluene, benzene, trifluoromethylbenzene, and anisole with benzenediazonium tetrafluoroborate in trifluoroethanol.³⁸ In this solvent, fluorobenzene and phenyl 2,2,2-trifluoroethyl ether are formed in addition to biphenyl derivatives from the arylation reactions.

The biphenyl isomer proportions show clearly that the reaction is not homolytic. The reaction rates with the four aromatic substrates are linearly dependent on the concentration of the substrates and the calculated second-order rate constants increase in the sequence $C_6H_5CF_3 < C_6H_5OCH_3 < C_6H_6 \sim C_6H_5CH_3$. The apparent decrease in the reactivity of anisole may be due to complex formation with BF_3 which is produced in the competitive Schiemann fluorination.

The results are consistent with an SN2-like mechanism (eq 4) or with an SNAr mechanism (eq 5). These two mechanisms differ only in that (4) is a two-step and (5) a three-step process involving an addition intermediate.



Mechanism 5 corresponds to the well-known Bunnett-Zahler mechanism,¹⁴ whereas (4) is unknown in nucleophilic aromatic substitution at the moment. Nevertheless, (4) is the more probable since the expected substituent effects in (5), *e.g.*, acceleration by $-M$ substituents (NO_2 , etc.) in the ortho and para positions, are absent in hydroxydediazonation.

The kinetic results are compatible with the classical SN1 mechanism only if, in step 6, $k_{-1}[N_2] \gg k_2[C_6H_5X]$, and, formally, this possibility cannot be excluded definitely. The logarithms of the rate constants for hydroxydediazonation of a series of substituted aryldiazonium ions have been compared with the π -energy difference between the diazonium ion and the respective aryl cation calculated by the HMO method.³⁹ A correlation is indicated, but large deviations (2 to 4 powers of ten) are found for *p*- NO_2 and *p*- C_6H_5 . A reevaluation⁴⁰ of these data gave the astonishing result that there is a perfect linear relation between all of Klasinc and Schulte-Frohlinde's values for π energies of the diazonium ions and those of the respective aryl cations! Therefore, these HMO data are not unambiguous evidence for the presence

(29) J. K. Bosscher and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **87**, 873 (1968); *J. Chem. Soc. B*, 1524 (1968); H. Cerfontain and A. Koeberg-Telder, *Recl. Trav. Chim. Pays-Bas*, **89**, 569 (1970).

(30) Review: H. G. Richey, Jr., and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 923.

(31) R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc. B*, 497 (1968).

(32) R. M. Cooper and M. J. Perkins, *Tetrahedron Lett.*, 2477 (1969).

(33) M. Kobayashi, H. Minato, E. Yamada, and N. Kobore, *Bull. Chem. Soc. Jap.*, **43**, 215 (1970); N. Kobori, M. Kobayashi, and H. Minato, *ibid.*, **43**, 223 (1970); N. Kamigata, M. Kobayashi, and H. Minato, *ibid.*, **45**, 2047 (1972).

(34) B. L. Kaul and H. Zollinger, *Helv. Chim. Acta*, **51**, 2132 (1968); B. Gloor, B. L. Kaul, and H. Zollinger, *ibid.*, **55**, 1596 (1972).

(35) E. S. Lewis and W. H. Hinds, *J. Amer. Chem. Soc.*, **74**, 304 (1952).

(36) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Amer. Chem. Soc.*, **91**, 419 (1969).

(37) E. S. Lewis, *J. Amer. Chem. Soc.*, **80**, 1371 (1958).

(38) P. Burri and H. Zollinger, to be published.

(39) L. Klasinc and D. Schulte-Frohlinde, *Z. Phys. Chem. (Frankfurt am Main)*, **60**, 1 (1968).

(40) E. Haselbach, University of Basle, personal communication.

of aryl cations; they are also consistent with an SN2-type transition state.

The same is true for the correlation which Schulte-Frohlinde and Blume⁴¹ found between the logarithms of rates of hydroxydediazoni-ation and the sum of Taft's substituent constants⁴² $\sigma_1 + |\sigma_M|$ (taking σ_M positive). This correlation demonstrates the dependence of the rate on the "strength" of the C₁-N_α bond, a result to be expected for SN1 and SN2 reactions. The six-membered ring of benzenediazonium chloride¹⁹ is distorted; the angle at C₁ is significantly larger than 120° (124.8°) and the C₁-C₂ bond is shorter (1.374 Å) than in benzene. This distortion is in the direction expected for a compound with an empty 2p orbital at C₁, *i.e.*, for an aryl cation. It is, however, present also in benzonitrile. The preexponential factors ($A = 10^{15} \text{ sec}^{-1}$) found by Schulte-Frohlinde⁴¹ appear not to favor an SN2 mechanism.

In conclusion, therefore, in our opinion there is no unambiguous evidence for a pure SN1 mechanism, but there exists a growing (although by no means complete) body of evidence for the occurrence of a bimolecular rate-limiting step. The existence of aryl cations in solution is therefore questionable, but they may be distinct intermediates in gas-phase reactions, *e.g.*, in the mass spectrometer.⁴⁰ EHMO, INDO, and MINDO/2 calculations⁴³ indicate a singlet and not a triplet ground state for the phenyl cation. A biradical-type structure, discussed by various authors on the basis of selectivity data for reactions in solution, is, however, not ruled out by Evleth's INDO calculations.

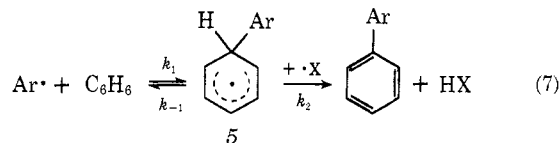
Homolytic Cleavage of the C₁-N_α Bond

Many reactions of diazonium salts and other diazo compounds are known in which it is probable that a homolytic cleavage of the C₁-N_α bond occurs. At the present time, however, only the decomposition of acylarylnitrosamines has been investigated to the extent that we may say, hopefully, that its mechanism, a multipathway reaction,⁵ is completely elucidated.

Related reactions also seem to follow multiple pathways. Small changes in the reactants, solvent, additives, etc., may change the rate, mechanism, and products drastically. Homolytic and heterolytic reaction mechanisms often resemble each other more closely than was previously thought. Some recent examples are: (a) the observation⁹ that either heterolytic or homolytic decomposition of some arenediazonium ions can occur in acidic methanol depending on the presence or absence, respectively, of oxygen; the rates of the two pathways differ only by a factor of about 2 and correlate linearly with the substituent effects of the (100% heterolytic) decomposition rates in acidic water. (b) Arylation of nitrobenzene with benzenediazonium ions in DMSO yields nitrobiphenyl isomers in proportions typical of a heterolytic process, whereas the same reaction with *p*-nitroben-

zenediazonium ion is clearly homolytic.³⁴ However, addition of *N,N*-diphenylhydroxylamine^{34,44a} or NaNO₂^{44b} to the reaction with unsubstituted benzenediazonium ion in DMSO increases the rate dramatically and yields nitrobiphenyl isomers in the proportions expected for an attack by phenyl radicals. (c) Decomposition of benzenediazonium ions in trifluoroethanol is a first-order heterolytic reaction which, however, becomes significantly faster, lower in order, and homolytic (as seen from the nature of the products) on the addition of a relatively small amount of pyridine.⁴⁵

As mentioned earlier, these observations can, in part, be explained by the concept of a *nucleofugal homolytic leaving group*, *i.e.*, an attack by a nucleophile X⁻ on the β nitrogen of the diazonium ion and its release as a radical ·X by fragmentation of the C₁-N_α and the N_β-X bonds (reaction 2 of this paper). *N,N*-Diphenylhydroxylamine and NaNO₂ are good nucleophiles and form good (*i.e.*, relatively stable) homolytic leaving groups, namely diphenyl nitroxide [(C₆H₅)₂NO·] + H⁺, and nitrogen dioxide, respectively. These products ·X in (2) are also more efficient "gegen-radicals" for the oxidation of the arylcyclohexadienyl radical 5, the intermediate of the subsequent homolytic aromatic substitution 7,



than those which are formed without such additives or with aroyl peroxides as radical sources. This becomes evident from the increased yield of biphenyl products as well as from a comparison of kinetic hydrogen isotope effects of arylations carried out with aroyl peroxides ($k_H/k_D = 6.6$)⁴⁶ with those for nitrite-assisted arylations in DMSO ($k_H/k_D = 1.01$ to 2.36)⁴⁷ and in "classical" (*i.e.*, heterogenous phase) Gomberg-Bachmann and acylarylnitrosamine^{4,48} reactions.

Pyridine is a good nucleophile, but a relatively poor homolytic leaving group; it therefore catalyzes decomposition, but the yield of biphenyl products is only slightly increased.⁴⁹ DMSO seems to be weakly nucleophilic toward diazonium ions since addition complexes and, in the presence of aromatic molecules, homolytic arylation products were detected only in the case of nitro-substituted arenediazonium ions.³⁴

Other examples of X⁻ and X are found in the var-

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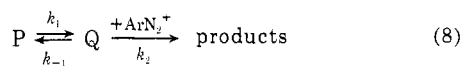
(48) Summaries: H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964); M. Kobayashi, H. Minato, N. Kobori, and E. Yamada, *Bull. Chem. Soc. Jap.*, **43**, 1131 (1970).

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ious protodediazoniating methods, *e.g.*, reduction by hypophosphorous acid ($X^- = \text{H}_2\text{PO}_2^-$),⁵⁰ methoxide ion,⁵¹ acetals, and others.^{52,53} The radical anion $\cdot\text{CH}_2\text{O}^-$ proposed by Bunnett⁵¹ actually forms a perfect nucleofugal homolytic leaving group, namely the formaldehyde molecule.

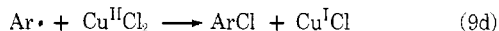
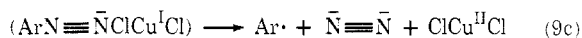
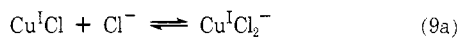
Therefore, for compounds X and X^- to be optimum catalysts for homolytic arylations, two functional properties are necessary: they must be good nucleophiles for the first step in (2) and they should yield energetically favorable radicals in the second step. A systematic investigation of these combined characteristics is desirable.

The homolytic cleavage mechanism 2 does not exclude the alternative route of direct electron transfer to the (free) diazonium ion established by R uchardt, *et al.*,⁵⁴ for Meerwein reductions. Hopefully, such investigations can be correlated with results obtained from detailed analyses of chain mechanism kinetics. Recently, the kinetics of the reaction of diazonium ions in aqueous solutions in the presence of nitrite ions⁵⁵ and in aqueous buffers (pH 9) with and without phenols as radical induction catalysts⁵⁶ were studied. In addition, the decompositions of diazonium ions in trifluoroethanol-pyridine mixtures,⁴⁵ in alcohols,⁵⁷ and in DMSO⁵⁸ have been investigated. The results are consistent with various chain mechanisms but not with a mechanism (eq 8) in which a

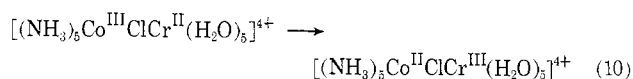


steady-state intermediate, Q, formed from an initiator, P, reacts with the diazonium ion in a nonchain process and where only the relation $k_{-1} > k_2[\text{ArN}_2^+]$ could explain a kinetic order lower than 1 in diazonium ion concentration.⁵⁵

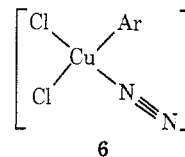
The catalytic function of cuprous salts in Sandmeyer reactions can be explained in a similar way, step 9b being rate limiting.^{13b,59} Step 9c has a sur-



prising resemblance to the electron-transfer reactions in $\text{Cr}^{\text{II}}\text{-Co}^{\text{III}}$ complexes which occur by the inner-sphere mechanism 10 proposed by Taube.⁶⁰ A simi-



lar mechanism was suggested for the reaction of diazonium ions with FeCl_2 .⁶¹ Unfortunately the influence of the transfer ligand on the rates of Sandmeyer reactions is known only qualitatively ($\text{Cl} < \text{Br} < \text{I}$, CN) but supports the inner-sphere mechanism. A mechanism (suggested by Vol'pin, *et al.*)⁶² involving complex 6 may look less reasonable for Cu^{I} complexes than for Ru^{II} complexes where outer-sphere reactions are predominant and back-donation takes place between Ru^{II} and nitrogen.



Yet another type of complex may be present in compounds $[\text{ArN}_2^+]_2[\text{ZnCl}_4^{2-}]$ which are used in technology if solid diazonium salts are required. They can be isolated with relatively little danger of explosion.^{7c} Their stability may be due to the formation of an inner complex (but without electron transfer, as Zn^{2+} cannot be oxidized) or simply because ZnCl_4^{2-} complexes are less nucleophilic than free chloride ions. In their investigations on diazonium carboxylates, R uchardt and Tan¹⁶ observed that the solid salts exploded and the ease with which this occurred increased with the nucleophilicity of the carboxylate used. This is consistent with the general experience^{13d} that, for safety reasons, tetrafluoroborates should be made if it is necessary to isolate a diazonium salt.

In connection with the industrial method of stabilizing diazonium ions, namely with arylsulfonic acids, ArSO_3H ,^{7d} it should be noted that present evidence points to the formation of charge-transfer complexes¹² and not diazosulfonates ($\text{ArN}_2\text{OSO}_2\text{Ar}'$) as previously thought.

Esr and CIDNP spectroscopy are obviously welcome tools for the detection and structural elucidation of radical intermediates in these reactions. Indeed, since 1966, the most important contributions to our knowledge of acylarylnitrosamine decomposition intermediates have come from esr.⁵

Other diazo reactions have recently been investigated with esr⁶³ and with CIDNP.⁶⁴ There is some direct evidence from ^{15}N CIDNP^{64f} and some indirect evidence from ^1H CIDNP^{64d} to suggest that arylidimine radicals ($\text{ArN}=\text{N}\cdot$) are formed and that

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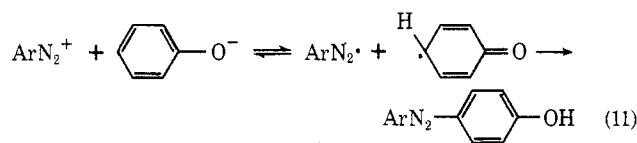
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in alkaline methanolic solution in the presence of phenol (conditions which favor radical formation) a homolytic diazo coupling reaction (eq 11) may take



place.^{64f} To the present author it seems probable that the precursor of the radical intermediates in (11) is a (covalent) aryl diazo ether.

¹³C CIDNP of *p*-methoxybenzenediazonium ions in CH₃O⁻-CH₃OH-CH₃CN gives a strong positive resonance at the C₁ position of the original diazonium ion which has been tentatively attributed to a polarized diazonium salt.^{64e} Polarographic data⁶⁵ are consistent with the primary formation of aryldiimine radicals.

Summarizing, it is obvious that we do not completely understand the mechanism(s) of homolytic decomposition of diazonium ions and related compounds (with the probable exception of the acylaryl-

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nitrosamine reactions). The concept of nucleofugal homolytic leaving groups and correlations with inorganic electron-transfer reactions help to rationalize the understanding of the catalytic effects in these reactions.

The question of whether there is a common intermediate for homolytic and heterolytic decompositions of diazonium ions is still open. It may be related to the N_α-N_β inversion in diazonium ions observed by Lewis,¹⁰ a problem which also applies to the fixation of N₂ molecules by transition metal complexes (end-on and edge-on complexes).^{11a,c}

As more elaborate quantum-chemical methods to consider solvation effects are not likely to be developed in the near future, we hopefully expect that the combined results from spectroscopy (esr and CIDNP) and from chain reaction kinetics will be instrumental in solving this and other problems in diazo chemistry.

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The Utilization of Sulfoximines and Derivatives as Reagents for Organic Synthesis

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Sulfoximine¹ chemistry began in 1950, when Whitehead and Bentley discovered that the sulfoximine of methionine is the agent responsible for the toxicity of wheat flour treated with nitrogen trichloride.² Such treatment had been widely practiced for many years.

Our work, which commenced in 1968, has focused on the utilization of sulfoximines and their derivatives as reagents for organic synthesis. Besides novelty, these compounds have great potential for synthetic applications; they enable things to be done easily which are difficult or impossible by other methods.

The sulfoximine functional group (Figure 1) is un-

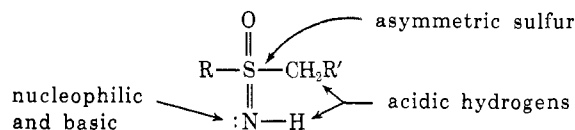


Figure 1. The sulfoximine functional group.

commonly versatile. It has acidic hydrogens on carbon and nitrogen, it is basic and nucleophilic at nitrogen, and it is potentially asymmetric.

As a model system and as a starting point for much of our work we have utilized *S*-methyl-*S*-phenylsulfoximine; this Account stresses chemistry emanating from this source. The most practical method for the synthesis of 1 and its *N*-methyl derivative 2 is illustrated in Scheme I.

Several methods can be used for the high-yield oxidation of thioanisole to methyl phenyl sulfoxide (3).³ We have routinely used a new laboratory meth-

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