The ratios of rate constants, k_{HForI}/k_{HFor} and k_{HForI_2}/k_{HForI}, have the values 4×10^2 and 5×10 M^{-1}, respectively. These, of course, have the significance of the iodide ion complexing constants of the formic acid catalyzed cleavage transition states. They are remarkably similar to the corresponding ratios for proton-catalyzed cleavage. One might have expected at least an electrostatic exaltation of the formation constants in the latter case. The fact that it is not observed suggests that the positive charge center and the mercury atom are quite widely separated in the transition state. A simple electrostatic calculation,[16] taking 78.5 as the appropriate dielectric constant,[17] gives 7 A as the distance at which the electrostatic potential energy between two electronic charges falls below RT, 600 cal mole^{-1}, near room temperature. Such a calculation can more easily underestimate than overestimate that distance because the effective dielectric constant can hardly be greater than, but may be less than that of pure water.[16] It is possible, of course, that this line of reasoning is entirely invalid because of differences in

charge distribution between the formic acid catalyzed transition state and that for hydronium ion catalysis. A distance of 7–10 A between the charge centers, if it can be accepted, is easily accommodated if a short chain of water molecules intervenes between the H_3O^+ unit and the substrate in the transition state.[3] It is hard to reconcile so large a distance with a transition state in which the H_3O^+ unit and the substrate are contiguous.

Experimental Section

The materials, solutions, and general techniques used in this investigation were essentially identical with those previously described.[8,14,18] The only new technique required is that for getting the zero-time optical density in experiments with high [I$^-$] and no added HgI_2. This is required in eq 8, and is not reliably given by plots such as those shown in Figure 1 because of the strong curvature near zero time. This problem was solved by extrapolating the line based on the points at high fractional conversion back to zero time. The logarithms of the differences between that line and the experimental points were a linear function of time, which could be extrapolated to zero time without difficulty. This zero-time difference was then added to the value obtained from the high conversion extrapolation to get $(D_\infty - D_0)$, from which D_0 itself is readily obtained.

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 200.
(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p 161.

(18) M. M. Kreevoy, J. Am. Chem. Soc., 81, 1009 (1959).

Radical Abstraction of Iodine from Aryl Iodides[1]

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Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912. Received August 8, 1966

Abstract: The main product from decomposition of bis(p-chlorobenzoyl) peroxide in a benzene solution of iodobenzene is p-chloroiodobenzene. Likewise, iodobenzene is the major product from thermolysis of benzoyl peroxide in a benzene solution of m-chloroiodobenzene. The formation of these and lesser products is best accounted for by direct iodine atom abstraction from aryl iodides by aryl radicals. The fact that no p-bromochlorobenzene is formed from decomposition of bis(p-chlorobenzoyl) peroxide in the presence of bromobenzene shows that p-chlorophenyl radicals failed to abstract bromine under the conditions employed.

Although radical abstraction of halogen atoms from alkyl halides of appropriate constitution is well recognized,[4a,b] the corresponding reaction of aryl halides does not appear to have been described.

We have found that radicals readily abstract iodine from aryl iodides. This reaction was recognized by observing p-chloroiodobenzene as a prominent product from the decomposition of bis(p-chlorobenzoyl) peroxide in a benzene solution containing iodobenzene. Other products detected, all in smaller yields than p-chloroiodobenzene, included 4-chlorobiphenyl, biphenyl, and chlorobenzene.

The formation of these products is readily accounted for by the set of reactions shown in Scheme I. All the reactions proposed in this scheme have ample precedent

in the modern literature, except for iodine atom transfer (reaction 2). The phenyl radical produced in reaction 2 appears as a reactant in reaction 4. The hydrogen donor in reaction 5 probably is, at least in part, the cyclohexadienyl radical shown as an intermediate in reaction 3 or the corresponding intermediate implied in reaction 4.

Decomposition of bis(p-chlorobenzoyl) peroxide in neat iodobenzene also afforded p-chloroiodobenzene as the principal product. No chlorobiphenyl was detected in this case, as might have been anticipated, but two isomeric 4-chloro-x'-iodobiphenyls and two isomeric iodobiphenyls were formed. The chloroiodobiphenyls obviously represent p-chlorophenylation of the iodobenzene, and the iodobiphenyls, phenylation by phenyl radicals generated as by-products of iodine atom transfer (reaction 2).

An independent demonstration of iodine abstraction involved decomposition of benzoyl peroxide in a benzene solution of m-chloroiodobenzene. The major product was iodobenzene, whose formation is attrib-

(1) Based in part on the Sc.B. thesis of C. C. W., June 1966. Research supported in part by the National Science Foundation.
(2) University of California, Santa Cruz.
(3) Brown University Undergraduate Research Assistant, 1965–1966.
(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) p 155; (b) p 255; (c) p 484.

uted to capture of an iodine atom from *m*-chloroiodo-benzene by phenyl radicals from decomposition of the peroxide. A lesser product was 3-chlorobiphenyl, which represents arylation of the benzene solvent by *m*-chlorophenyl radicals generated in the iodine atom transfer.

Attempts to deomonstrate bromine atom transfer in analogous experiments were fruitless. No *p*-bromo-chlorobenzene was detected as a product from decomposition of bis(*p*-chlorobenzoyl) peroxide in the presence of bromobenzene, either neat or in benzene solution. Nor was *p*-bromochlorobenzene formed when this peroxide was decomposed in a benzene solution of 1,2,3-tribromobenzene.

The foregoing experiments are summarized in Table I.

Table I. Summary of Experiments

Expt	Reactants (mmoles)	Products (moles per mole of peroxide)
1	Bis(*p*-chlorobenzoyl) peroxide (1.0)	*p*-Chloroiodobenzene (0.29)
	Iodobenzene (1.0)	*p*-Chlorobiphenyl (0.25)
	Benzene (56.3)	Chlorobenzene (0.09)
		Biphenyl (0.08)
2	Bis(*p*-chlorobenzoyl) peroxide (1.0)	*p*-Chloroiodobenzene (0.67)
	Iodobenzene (5.0)	*p*-Chlorobiphenyl (0.16)
	Benzene (56.3)	Chlorobenzene (0.06)
		Biphenyl (0.22)
3	Bis(*p*-chlorobenzoyl) peroxide (2.0)	*p*-Chloroiodobenzene (0.76)
	Iodobenzene (44.9)	*x*-Iodobiphenyl (0.25)
		y-Iodobiphenyl (0.14)
		4-Chloro-*x'*-iodobiphenyl (0.06)
		4-Chloro-*y'*-iodobiphenyl (0.02)
4	Benzoyl peroxide (1.0)	Iodobenzene (0.43)
	m-Chloroiodobenzene (1.0)	Biphenyl (0.32)
	Benzene (169)	Chlorobenzene (0.04)
		m-Chlorobiphenyl (0.17)
5	Bis(*p*-chlorobenzoyl) peroxide (1.0)	*p*-Chlorobiphenyl (0.43)
	Bromobenzene (1.0)	Chlorobenzene (0.11)
	Benzene (56.3)	
6	Bis(*p*-chlorobenzoyl) peroxide (2.0)	Chlorobenzene (0.08)
	Bromobenzene (47.7)	U. P.[a] 1 (0.32)
		U. P.[a] 2 (0.30)
		U. P.[a] 3 (0.50)
		U. P.[a] 4 (0.30)
7	Bis(*p*-chlorobenzoyl) peroxide (1.0)	*p*-Chlorobiphenyl (0.39)
	1,2,3-Tribromobenzene (1.0)	Chlorobenzene (0.09)
	Benzene (56.3)	

[a] U. P. signifies unidentified product (listed in order of retention time by gas–liquid partition chromatography).
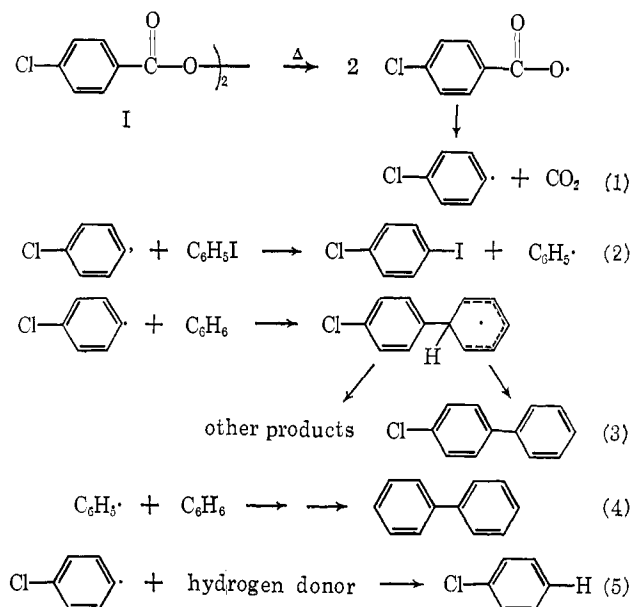
Discussion

As mentioned above, the formation of *p*-chloroiodo-benzene from decomposition of bis(*p*-chlorobenzoyl) peroxide in the presence of iodobenzene, and of iodo-benzene from benzoyl peroxide and *m*-chloroiodoben-zene, are readily accounted for by postulation of iodine atom transfer from aryl iodides to aryl radicals (*e.g.*, reaction 2, Scheme I).

It is possible to dispose of two conceivable alternative interpretations. One is that photolysis of the aryl iodides, to form aryl radicals and iodine atoms,[5] occurs simultaneously with pyrolysis of the peroxide and that

(5) W. Wolf and N. Kharasch, *J. Org. Chem.*, 30, 2493 (1965).

Scheme I

$$\text{Cl---C}_6\text{H}_4\text{---C(=O)---O---]}_2 \xrightarrow{\Delta} 2 \text{ Cl---C}_6\text{H}_4\text{---C(=O)---O·}$$

$$\text{Cl---C}_6\text{H}_4\text{·} + CO_2 \quad (1)$$

$$\text{Cl---C}_6\text{H}_4\text{·} + C_6H_5I \longrightarrow \text{Cl---C}_6\text{H}_4\text{---I} + C_6H_5\text{·} \quad (2)$$

$$\text{Cl---C}_6\text{H}_4\text{·} + C_6H_6 \longrightarrow \text{Cl---C}_6\text{H}_4\text{---C}_6\text{H}_6\text{·} \quad$$

other products $\quad$ Cl---C$_6$H$_4$---C$_6$H$_5$ $\quad$ (3)

$$C_6H_5\text{·} + C_6H_6 \longrightarrow \longrightarrow \text{C}_6\text{H}_5\text{---C}_6\text{H}_5 \quad (4)$$

$$\text{Cl---C}_6\text{H}_4\text{·} + \text{hydrogen donor} \longrightarrow \text{Cl---C}_6\text{H}_4\text{---H} \quad (5)$$

the radicals in the resulting melange recombine in various combinations which include the transiodination products. The primary grounds for dismissing this interpretation is that light was excluded from our reactions by careful wrapping of the flasks with aluminum foil.

It is conceivable that transiodination may have been initiated by attack, *e.g.*, of *p*-chlorophenyl radical on the *carbon* of iodobenzene which bears the iodine atom. The resulting aryliodocyclohexadienyl radical (II) might then lose its iodine atom to a *p*-chlorophenyl radical, either by direct radical attack on iodine in II or by spontaneous homolysis to form 4-chlorobiphenyl and

II
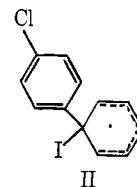
an iodine atom which then combined with a *p*-chloro-phenyl radical encountered in the medium. A mechanism of this general type possibly obtains in the light-catalyzed chlorodebromination and bromodeiodination reactions which occur between aryl bromides and elemental chlorine or aryl iodides and elemental bromine.[6] However, this mechanism for iodine transfer can be discarded because it requires formation of as much *p*-chlorobiphenyl as *p*-chloroiodobenzene from decomposition of bis(*p*-chlorobenzoyl) peroxide in neat iodobenzene. In fact, no *p*-chlorobiphenyl could be detected as a product of that reaction.

In its detailed character, the transiodination reaction may be a one-step radical displacement on iodine, or it may comprise two steps and involve a diaryliodine intermediate (*e.g.*, III). This intermediate might either

III
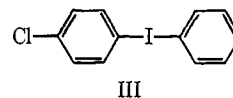
(6) B. Miller and C. Walling, *J. Am. Chem. Soc.*, 79, 4187 (1957); B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *ibid.*, 84, 158 (1962).

revert to the species from which it was formed (e.g., iodobenzene and p-chlorophenyl radical) or progress to a new product pair (p-chloroiodobenzene and phenyl radical).

Evidence that diphenyliodine is formed on electroreduction of diphenyliodonium ion has been presented by Bachofner, Beringer, and Meites.[7] Their efforts to prepare diphenyliodine by controlled-potential electrolysis of diphenyliodonium p-toluenesulfonate were unsuccessful. However, the products of this electrolysis (iodobenzene, benzene, and biphenyl) were consistent with fission of diphenyliodine to iodobenzene and phenyl radical.

There are also indications that diphenyliodine is formed by electron transfer from the malonic ester anion to diphenyliodonium ion.[8] Whether formed by electrolytic reduction or by electron transfer from an anion, diphenyliodine appeared to be a very short-lived species.

Diaryliodines are feasible intermediates in the iodine-transfer reactions we have observed.

Reactivity in Transiodination. The fact that radical abstraction of iodine occurs under conditions in which radical abstraction of bromine does not occur suggests that reactivity in abstraction of halogen atoms is related to the dissociation energy of the bond being broken. For radical abstraction of halogen from aliphatic sites, the reactivity order I > Br > Cl has been noted.[4b] Walling has commented that increasing reactivity in such reactions parallels decreasing strength of the C–X bond involved.[4b] This similarity between aromatic and aliphatic systems would independently suggest a similarity of mechanism, and thus is further support for the mechanism of direct iodine atom abstraction which we have proposed.

From the results of expt 2 (Table I), it is possible to make a rough estimate of the reactivity of p-chlorophenyl radical in abstracting iodine from iodobenzene relative to arylating benzene. Taking into account the yields of p-chloroiodobenzene and p-chlorobiphenyl and the amounts of iodobenzene and benzene present in the reaction mixture, one estimates that the rate coefficient for iodine capture is 50 times greater than that for p-chlorophenylation of benzene. Inasmuch as iodobenzene is phenylated about 1.8 times faster than benzene,[4c] the rate of iodine abstraction from iodobenzene is very roughly about 30 times that of arylation of its nucleus.[9]

Uncertainties in these estimates enter from at least two sources. One is that whereas iodine capture doubtless has a simple rate law, arylation is a multistep reaction whose rate is determined not only by the rate of the

(7) H. E. Bachofner, F. M. Beringer, and L. Meites, *J. Am. Chem. Soc.*, 80, 4269, 4274 (1958).

(8) F. M. Beringer and P. S. Forgione, *Tetrahedron*, 19, 739 (1963).

(9) It is curious that abstraction of iodine from aryl iodides was not observed in the course of determinations of the rate of arylation of iodobenzene (relative to benzene).[10,11] The reason is mainly that only arylation of iodobenzene by unsubstituted phenyl radicals was studied kinetically. In this special case, the products of iodine transfer are the same as the reactants. However, Dannley, Gregg, Phelps, and Coleman[11] record an experiment in which 0.1 mole of benzoyl peroxide was decomposed in the presence of 0.2 mole of (neat) iodobiphenyl mixture. They were able to recover only 20% of the iodobiphenyls introduced, contaminated with some biphenyl. It is probable that iodobenzene and biphenyl were major products of the reaction that occurred.

(10) D. R. Augood, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3412 (1953).

(11) R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps, and C. B. Coleman, *J. Am. Chem. Soc.*, 76, 445 (1954).

initial attack of aryl radical on aromatic carbon but also by the availability of hydrogen atom acceptors which affect partitioning of the resulting cyclohexadienyl radical between hydrogen loss and other fates.[12] Also, relative rates of arylation of benzene derivatives vary somewhat according to the substituents present in the arylating radical.

Experimental Section

Materials. Bis(p-chlorobenzoyl) peroxide was prepared from p-chlorobenzoyl chloride and aqueous alkaline peroxide, according to the method of Gelissen and Hermans.[13] The product was isolated as tiny white plates, mp 142° dec (lit.[13] 137–138° dec). Benzoyl peroxide was from Eastman Kodak Co., mp 106–107° dec (lit.[14] 105–106° dec). Iodobenzene from commerical sources was found unsuitable for use because of a major impurity, obvious in both its gas-liquid partition chromatogram and its infrared spectrum. Iodobenzene was prepared by diazotization of aniline and treatment with aqueous potassium iodide, according to the method of Lucas and Kennedy.[15] The product had bp 186–187°, was pure by glpc, and gave an infrared spectrum identical with that published by the National Bureau of Standards.[16] m-Chloroiodobenzene was from Eastman Kodak Co., and was shown to be pure by glpc at 90° through a 4-ft column packed with 10% SE-30 on Chromosorb P. Bromobenzene was from Eastman Kodak Co. and was shown to be pure by glpc under the conditions described just above. 1,2,3-Tribromobenzene, mp 87–88° (lit.[17] 87.8°), was generously provided by Miss Rae R. Victor. Benzene was Fisher, Certified reagent grade.

Authentic samples used in product identifications were from the following sources. p-Chloroiodobenzene was from Eastman Kodak Co., mp 54–55° (lit.[18] 56.2°). Biphenyl was a sample available in the laboratory, recrystallized twice, mp 69.5–70.5°. m-Chlorobiphenyl, prepared from m-chloroaniline by a Gomberg reaction, was generously provided by Dr. Hiroaki Takayama. p-Chlorobenzoic acid was available in the laboratory. After two recrystallizations, it had mp 240.5–241.5° (lit.[19] 241.5°). Benzoic acid was a sample available in the laboratory, once recrystallized, with mp 121–122°. p-Chlorobromobenzene was from Eastman Kodak Co., mp 66–67° (lit.[20] 68°).

General Experimental Procedure. All experiments were performed in a 50-ml, round-bottomed flask equipped with reflux condenser and capped with a calcium chloride tube. The flask was completely wrapped in aluminum foil and was set in a steam bath. The aryl iodide was weighed in a tared, 5-ml beaker and quantitatively transferred to the reaction vessel by rinsing with the solvent. The aryl peroxide was weighed on a tared piece of glazed paper and added to the reaction flask. The solution was maintained at steam bath temperature (the reflux temperature of the benzene solution in the case of reactions 1, 2, 4, 5, and 7) for 5 hr.

After cooling, exactly 1.00 mmole of an internal standard was added to the reaction solution (bromobenzene in reactions 1–4, iodobenzene in reactions 5–7). This reaction solution was analyzed directly by glpc. An aliquot of 50–100 μl was injected onto an F & M Model 500 thermal conductivity chromatograph, using a 4-ft column packed with 10% SE-30 on Chromosorb P, a helium flow of about 60 cc/min, an injection port temperature of about 130°, and an initial column temperature of 60°. Typically, products were eluted in the order: benzene, chlorobenzene, bromobenzene, iodobenzene, chloroiodobenzene, biphenyl, chlorobiphenyl, followed by more highly substituted biphenyls. Typically, the column temperature was maintained at 60° for the benzene, chlorobenzene, and bromobenzene peaks, then programmed manually to 90° for the iodobenzene, chloroiodobenzene, and biphenyl peaks, then raised to 120° for the substituted bi-

(12) D. F. DeTar and R. A. J. Long, *ibid.*, 80, 4742 (1958).

(13) H. Gelissen and P. H. Hermans, *Ber.*, 58, 285 (1925).

(14) D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, 77, 6370 (1955).

(15) H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 351.

(16) E. K. Plyler, H. C. Allen, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, 58, 256 (1957).

(17) G. Körner and Contardi, *Atti Accad.. Lincei*, [5] 22I, 830 (1913).

(18) K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, 65, 199 (1935).

(19) N. V. Sidgwick and E. K. Ewbank, *J. Chem. Soc.*, 119, 981 (1921).

(20) D. Vorländer, *Ber.*, 71, 1688 (1938).

phenyls. This allows all the peaks to be well shaped and still well separated.

Yields of all products were derived by comparison of peak areas with the peak area of the internal standard. Standardizations were made in the form of calculated molar-response factors. These were determined for each individual product by analysis of an accurately known mixture of the product in question and the internal standard, chromatographed under conditions close to those encountered in a typical reaction analysis.

Various products from these reactions were isolated by preparative glpc. The column found most effective was a 4.5 ft $\times$ $^3/_8$ in. aluminum column packed with 17% Carbowax 200 M on Chromosorb P, using a helium flow of about 100 cc/min. The reaction solution was concentrated to about 1 ml, all of which was injected. Collections were made in U tubes cooled in Dry Ice–isopropyl alcohol. The resulting samples were then analyzed for melting point, infrared spectrum, and/or mass spectrum, as described below.

Identification of Products. *p*-Chloroiodobenzene was isolated from expt 1 and 3, Table I. The sample from expt 1 had mp 52–53° and both samples had infrared spectra in excellent agreement with that of an authentic sample.

p-Chlorobiphenyl was isolated from expt 1. The sample had mp 72–75° (lit.[21] 77.2°) and an infrared spectrum with strong absorptions at 692, 760, and 833 cm^{-1}. Conley[22] lists absorptions at 690–710 and 730–770 cm^{-1} for a monosubstituted benzene, and at 810–833 cm^{-1} for a 1,4-disubstituted benzene. Thus a 4-substituted biphenyl is suggested. Mass spectrography showed parent peaks at *m/e* 188 and 190, and other prominent peaks at 152–153 and 76.[23]

(21) C. H. Penning, *Ind. Eng. Chem.*, **22**, 1180 (1930).

(22) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, p 107.

(23) We are grateful for the assistance of Mr. Albert H. Smith with the mass-spectrometric analyses.

These data are clearly indicative of a chlorobiphenyl.

Biphenyl was isolated from expt 1 and 4. The sample from expt 1 had mp 68–69°, that from expt 4 had mp 66–67°. Both samples gave infrared spectra which agreed excellently with the spectrum of an authentic sample.

Iodobenzene was isolated as a product from expt 4. It was identified by the identity of its infrared spectrum with that of an authentic sample.

m-Chlorobiphenyl was isolated from expt 4 and was identified by the identity of its infrared spectrum with that of an authentic sample.

Two isomeric iodobiphenyls, clearly separated by glpc, were isolated from expt 3. The two samples gave nearly identical mass spectrograms. The parent peak was at *m/e* 280 with prominent peaks at 152–153 and 76–77.

Two isomeric chloroiodobiphenyls, clearly separated by glpc, were isolated from expt 3. Mass spectrometric evidence from both samples showed parent peaks at *m/e* 314 and 316. The fragmentation patterns were not identical, however. One isomer showed significant peaks at 280 (I–C_6H_4–C_6H_5), 152 (C_6H_4–C_6H_4), and 76 (C_6H_4). The other isomer showed its prominent peaks at 186, 187, 188, and 189 (C_6H_4–C_6H_4Cl and $C_{12}H_7Cl$), 152 (C_6H_4–C_6H_4), and 76 (C_6H_4).

Benzoic acid was isolated from expt 4. The sample had mp 107–115° and its infrared spectrum agreed well with that of an authentic sample.

p-Chlorobenzoic acid was isolated as a precipitate from expt 1. The sample had mp 236–238° and gave an infrared spectrum which agreed excellently with that of an authentic sample.

p-Chlorobromobenzene was shown to be nonexistent as a product of reactions 5–7 by retention-time evidence. Addition of authentic *p*-chlorobromobenzene to these reaction solutions caused the appearance of a new peak in the gas–liquid partition chromatograms where nothing was previously observable.

The Iodination of Coordinated Imidazole[1]

Don G. Lambert and Mark M. Jones

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203. Received July 29, 1966

Abstract: When imidazole is coordinated at the "pyridine" nitrogen (3 position) to nickel(II), its rate of iodination follows a law different from that for the iodination of free imidazole. The reaction is first order in iodine and first order in nickel complex; no term corresponding to a self-catalyzed path is found. For variation of iodide or hydrogen ion concentration, the results for the nickel(II) complex are more complicated than those for free imidazole. The results can be correlated with a mechanism involving reaction of both [Ni(ImH)]$^{2+}$ and [Ni(Im)]$^+$ with the iodine molecule. The energy and entropy of activation is the same, within experimental error, for the uncatalyzed reaction of the free ligand as for the reaction of the coordinated ligand. The principal consequences of these results for the mechanism of the iodination of imidazole itself is to rule out the iodonium ion as a probable attacking species.

I midazole is one of the few heterocyclic molecules for which extensive kinetic data on substitution reactions are available.[2] The iodination of the ligand has been examined by two groups of workers,[3,4] and the deuterium isotope effect has also been studied.[5] In addition, complexes of the ligand with nickel(II)

are quite stable.[6] As part of a general program involving comparison of the reactivity of the coordinated and uncoordinated ligand,[7] the iodination of the nickel(II) complex of imidazole was studied.

Experimental Section

Materials. The imidazole, recrystallized three times from benzene, melted at 88.5° (lit.[3,4] 88.0, 89.0°). All other chemicals

(1) Grateful acknowledgment is made of the support of this work by the Air Force Office of Scientific Research through Grant AF-AFOSR-630-64.

(2) For a summary, see W. Adam and A. Grimison, *Tetrahedron*, **22**, 835 (1966).

(3) J. H. Ridd, *J. Chem. Soc.*, 1238 (1955).

(4) J. D. Vaughan, D. G. Lambert, and V. L. Vaughan, *J. Am. Chem. Soc.*, **86**, 2857 (1964).

(5) A. Grimison and J. H. Ridd, *J. Chem. Soc.*, 3019 (1959).

(6) (a) B. L. Michel and A. C. Andrews, *J. Am. Chem. Soc.*, **77**, 5291 (1955); (b) N. C. Li, T. L. Chu, C. T. Fujii, and J. M. White, *ibid.*, **77**, 859 (1955).

(7) M. M. Jones in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 48, American Chemical Society, Washington, D. C., 1965, pp 153–162.