Activations, Table II.—In preliminary experiments, 2.5-g samples of wet manganese dioxide were azeotropically activated using ethyl ether, carbon tetrachloride, chloroform, or propionitrile. After a suitable azeotroping period, as judged by the appearance of the manganese dioxide, excess benzyl alcohol was added, with stirring for about 0.5 hr. Following filtration and solvent removal, benzaldehyde was detected by conversion to the 2,4-dinitrophenylhydrazone. In each case a substantial amount of the derivative formed, indicating some degree of activation. The wet catalyst, unactivated, gave no detectable benzaldehyde under these conditions.

The extractive activations with ethyl ether and acetonitrile were performed as follows. Wet manganese dioxide (25-g samples) was stirred vigorously with ten 200-ml portions or five 200-ml portions of ether or acetonitrile, respectively. Stirring was continued for about 5 min for each portion of fresh solvent. Spent solvent was decanted prior to addition of fresh solvent. To the activated materials, in benzene solvent, were then added 3-g samples of benzyl alcohol. After 1 hr, the yield of benzaldehyde, as the 2,4-dinitrophenylhydrazone, was determined. Oxidizing power was determined in comparison with benzene-azeotroped material, on the basis of 10.5 g of active material in each case.

Registry No.—Manganese dioxide, 1313-13-9.

Acknowledgment.—The technical assistance of Mrs. Nancy N. Arnold is gratefully acknowledged.

Catalytic Decomposition and Chemical Reduction of Diaryliodonium Salts. Reactions Involving Ligand Transfer[1]

F. MARSHALL BERINGER AND PETER BODLAENDER

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

Received August 26, 1968

Copper(I) salts have been shown to be extremely efficient catalysts for the decomposition of diaryliodonium salts.[2] A study of the reaction of iodonium salts with metal salts more strongly reducing than copper(I), *i.e.*, titanium(III) and chromium(II), has been initiated, and the copper-catalyzed reaction has been further investigated.

Titanium(III) chloride was found to be an efficient catalyst for the decomposition of diphenyliodonium chloride (Table I). The reaction in water proceeds to completion with 0.06 equiv of titanium(III) chloride, yielding only iodobenzene and chlorobenzene without consuming titanium(III). The same reaction in methanol, however, went only 39% to completion, with complete consumption of catalyst (Table I). The main products were iodobenzene and benzene, along with small quantities of chlorobenzene and biphenyl.

Polarographic studies[3] of iodonium salts had previously revealed that diphenyliodonium cations may accept one electron ($E_{1/2} = -0.2$ V *vs.* sce) forming diphenyliodine, which is unstable and rapidly decomposes to iodobenzene and phenyl free radicals. Further, the reactions of diphenyliodonium salts have been intensively studied, and on the basis of several factors (product distribution, steric effects, dehydrogenation of solvent, effect of oxygen, polymerization of styrene) an initial step of electron transfer from carbanion to iodonium ion has been proposed.[4a,5] In the light of these earlier conclusions and in light of the above results with titanium(III) chloride, a mechanism to explain this catalysis is now proposed.

The reaction is formulated as initiated by an electron transfer from a titanium(III) species[6] to yield unstable diphenyliodine and a titanium(IV) species.[6] In turn, diphenyliodine decomposes to iodobenzene and a phenyl free radical,[3] whose fate is determined by the solvent and other reactants. In water the phenyl radicals react exclusively with a titanium(IV) species, forming chlorobenzene and regenerating titanium(III) by a ligand-radical transfer process.[7] In methanol, however, the predominant path is hydrogen abstraction from solvent; regeneration of titanium(III) is therefore much less efficient. The reaction in water, in the presence of acrylonitrile, yielded polyacrylonitrile. Polymerization did not take place under identical conditions in the absence of iodonium salt. This observation is in accord with the postulated existence of phenyl free radical intermediates. Product distribution studies of the titanium(III)-catalyzed decomposition of unsymmetrical 4-methoxydiphenyliodonium chloride in water showed the ratio of cleavages of C_6H_5–I/$CH_3OC_6H_4$–I to be 1.4. This insensitivity of carbon–iodine bond cleavage to polar substituents on the phenyl ring has been taken to indicate nonpolar bond fission.[4,8] The yield of chlorobenzene, from reactions run in methanol, was independent of acid and chloride ion concentrations but did depend on the Ti(IV)/Ti(III) ratio (Table I). Addition of $TiCl_4$ to methanol results in the formation of $TiCl_2(OMe)_2$.[9] The resulting increased concentration of titanium(IV)-bound chloride, which can undergo ligand-radical transfer to a phenyl radical, is reflected in significantly increased yields of chlorobenzene. As expected, anisole was not detected since methoxide does not readily undergo ligand-radical transfer.[7a] To the knowledge of the authors ligand-radical transfer processes involving titanium salts have not previously been described.

Chromium(II) chloride, a more powerful reducing agent than titanium(III), yielded mainly iodobenzene

---

[1] This paper is largely based on part II of a dissertation submitted by P. Bodlaender in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1967.

[2] F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

[3] H. E. Bachofner, F. M. Beringer, and L. Meites, *J. Amer. Chem. Soc.*, **80**, 4269, 4274 (1958).

[4] (a) F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, 4442 (1964); (b) M. Swarc, C. H. Leigh, and A. H. Schon, *J. Chem. Phys.*, **19**, 657 (1951); (c) R. F. Bridger and G. A. Russel, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

[5] (a) F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963); (b) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3417 (1963).

[6] Information about the stability constants of titanium chloride complexes is extremely limited. Indications are that titanium(III) chloride, in aqueous solutions under the conditions of the reactions here studied, exists mainly as $TiCl^{2+}$, a partially hydrolyzed species. The situation for titanium(IV) chloride is even less clear but the participation of $Ti(OH)_2Cl_2$ or $TiOCl_2$ seems to be a possibility: L. G. Sillen and A. E. Martell, Special Publication No. 17, The Chemical Society, Burlington House, London, 1966; F. R. Duke and P. R. Quinney, *J. Amer. Chem. Soc.*, **76**, 3800 (1954); A. G. Stromberg and A. I. Kartushenskaya, *Zh. Fiz. Kihm.*, **35**, 1058 (1961); B. I. Nabivanets, *Zh. Neorg. Khim.*, **7**, 412, 417 (1962).

[7] (a) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962); (b) J. K. Kochi and R. V. Submaranian, *J. Amer. Chem. Soc.*, **87**, 1508, 4855 (1965); (c) A. H. Lewin, A. H. Dinwoodie, and T. Cohen, *J. Org. Chem.*, **32**, 3844 (1964).

[8] M. C. Caserio, D. L. Glusker, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 336 (1959).

[9] R. Feld and P. L. Cowe, "The Organic Chemistry of Titanium," Butterworth and Co. Ltd., London, 1965, pp 1, 20, L54.

TABLE I

PRODUCTS OF REACTIONS OF DIPHENYLIODONIUM CHLORIDE WITH TITANOUS CHLORIDE[a]

Solvent	$[TiCl_3]/[-I^+-]$	Additive	Reaction,[b] %	Product yield, %[c,d] PhCl	PhH	Ph_2
Water	0.10		100	100		
Water (1 *N* HCl)	0.06		100	100		
Methanol	1.0		97[e]	10	86	4
Methanol	0.30		85[f]	8	88	4
Methanol	0.21		70	13	83	4
Methanol	0.06		39[g]	12	82	6
Methanol	1.0	HCl[h]	89[i]	10	87	3
Methanol	1.0	LiCl[j]	100	6	88	6
Methanol	1.0	$TiCl_4$[k]	93	27	69	4
Methanol	1.0	(O_2)[l]	100	20	76	4
Methanol	0.09	(O_2)[m]	60[n]	46	48	6
Water	0.10	$CH_2{=}CHCN$[o]	47	Polyacrylonitrile (63%)[p]		

[a] Reactions were run in an inert atmosphere and deaerated solvents at 65° for 24 hr. [b] Determined from PhI analysis and also by the recovery of iodonium salt as the iodide. When both procedures were used on the same run, they agreed to within 2%. $TlCl_3$ does not react with PhI under the conditions of the reaction. [c] Determined by vpc. [d] Normalized to 100%. Total recovery was 100% except where noted. [e] Total recovery was 90%. [f] Total recovery was 96%. [g] Total recovery was 85%. [h] 1.0 mol of HCl/mol of $Ph_2I^+Cl^-$. [i] Total recovery was 91%. [j] 0.6 mol of LiCl/mol of $Ph_2I^+Cl^-$. [k] 0.16 mol of $TiCl_4$/mol of $Ph_2I^+Cl^-$. [l] Solvent was not degassed, and the reaction was left open to the atmosphere. [m] $TiCl_3$ was exposed to atmosphere before using. [n] Yield is based on the weight of starting acrylonitrile. [o] 1.0 mol of $CH_2{=}CHCN$/mol of $Ph_2I^+Cl^-$. Reaction was run at 80° for 8 hr. In the absence of iodonium salt, polymerization was not observed. [p] Total recovery was 93%.

and benzene with smaller quantities of chlorobenzene and biphenyl from reactions with diphenyliodonium chloride in water (Table II). Chromium(II) is irreversibly oxidized during the course of the reaction. Stoichiometry requiring a 2:1 ratio of metal salt to diphenyliodonium chloride is indicated by the results summarized in Table II. A proposed mechanism is based on established iodonium salt chemistry and on the currently accepted explanation of the reduction of alkyl halides by chromium(II) salts.[10] As with titanium(III), a one-electron transfer from a low-valent metal complex to the iodonium cation results in the initial formation of diphenyliodine, which decomposes rapidly to iodobenzene and phenyl free radicals. The phenyl radical may be captured by a second chromium(II) ion to furnish an organometallic intermediate, which on protonation yields benzene and the chromium(III) ion; alternatively, the radicals may dimerize to form biphenyl. The use of less than the stoichiometrically required amount of reducing agent caused a significant increase in the yield of biphenyl. This observation seems to rule out a coupling reaction involving a diphenylchromium intermediate[11] and indicates that capture of phenyl radicals by chromium(II) and the dimerization reaction are competitive reactions, with the former being favored. Further, material balance of iodobenzene indicates no loss of iodobenzene, thus excluding a coupling involving iodobenzene.

TABLE II

PRODUCTS OF REDUCTION OF DIPHENYLIODONIUM CHLORIDE WITH CHROMOUS CHLORIDE IN WATER[a]

$[CrCl_2]/[-I^+]$	Additive	Reaction,[b] %	Product yield, %[c] PhCl	PhH	Ph_2
1.0		61[d]	11	50	39
2.0		85	9	84	7
2.0	LiCl[e]	82[f]	14	76	10
2.0	$CrCl_3$[g]	85	14	74	12
2.0[h]	(O_2)	83	29	63	8
2.0[i]		96	44	51	5

[a] Reactions were run for 1 hr at 95°, in an inert atmosphere and deaerated solvents. [b] Determined from PhI analysis and also by the recovery of iodonium salt as the iodide. When both procedures were used on the same run, they agreed to within 5%. [c] Determined by vpc. Normalized to 100%. Total recovery was 96–100% except where noted. [d] Total recovery was 92%. [e] 1.0 mol of LiCl/mol of $Ph_2I^+Cl^-$. [f] Total recovery was 80%. [g] 0.32 mol of $CrCl_3$/mol of $Ph_2I^+Cl^-$. [h] The concentration of chromium(II) was determined for the fresh uncontaminated solution which was then briefly exposed to the atmosphere. [i] Chromium(II) chloride solution showed signs of decomposition.[j] [j] J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

The yields of chlorobenzene were independent of the concentration of LiCl and $CrCl_3$ but did increase if solutions containing chromium(II) were briefly exposed to air prior to the reaction or if solutions were used which showed signs of decomposition. In the latter two cases the solutions were at a higher pH.[12] This behavior was also observed in the titanium(III) system. Whether a pH-dependent ligand-radical transfer process is operating, possibly involving oxygenated complexes of chromium[13] or titanium, is not clear at this time. The observation by Kochi and Davis[10b] that benzyl chloride is regenerated during the reaction with chromium(II) chloride may be relevant.

Mechanisms previously postulated[3,4a,8] for the copper-catalyzed decomposition of diaryliodonium salts were analogous to those for the well-established copper-catalyzed reactions of aryldiazonium salts in the Sandmeyer and Meerwein reactions.[14] The suggested mechanistic path involved an electron transfer from copper(I) to the iodonium cation, with subsequent homolytic cleavage of the aryl–iodine bonds, followed by ligand-radical transfer from copper(II) to the aryl radical, with regeneration of copper(I). Evidence for

---

(10) (a) D. H. R. Barton, N. K. Basu, R. H. Hesse, F. S. Morehouse, and M. M. Pechet, *J. Amer. Chem. Soc.*, **88**, 3017 (1966); (b) J. K. Kochi and D. D. Davis, *ibid.*, **86**, 5264 (1964); (c) J. K. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965); (d) C. E. Castro, *ibid.*, **83**, 8262 (1961).

(11) M. Tsutsui and H. Zeiss, *ibid.*, **81**, 1367 (1959).

(12) See Table II, footnote *j*.

(13) M. Ardon and G. Stein, *J. Chem. Soc.*, 2095 (1956).

(14) (a) N. A. Cowdry and D. S. Davies, *Quart. Rev.* (London), **6**, 358 (1952); (b) J. K. Kochi, *J. Amer. Chem. Soc.*, **79**, 2942 (1957); (c) S. C. Dickerman, K. Weiss, A. K. Ingberman, *ibid.* **80**, 1904 (1958); (d) G. N. Schrauzer, *Ber.*, **94**, 1891 (1961).

TABLE III

PRODUCTS OF COPPER-CATALYZED DECOMPOSITION OF DIPHENYLIODONIUM CHLORIDE[a]

Solvent	$[CuCl^-]/[-I^+-]$	Cupric salts	% yield[b,c]	
			PhCl	PhOH
Water	0.031		95	5
Water (0.25 *N* HCl)	0.031		100	
Methanol	0.020		100	
Acetone	0.027		100	
Water	0.028	$CuSO_4$[d]	89	11
Water	0.030	$Cu(NO_3)_2$[e]	89	11
Water[f]		$Cu(NO_3)_2$[g]	86	14
Water[h]	0.030		96	4

[a] Reactions were run at 60–65° for 1 hr in an inert atmosphere and deaerated solvents. Reactions went 100% to completion as determined from analyses for iodobenzene and for unreacted iodonium salt. [b] Determined by vpc; neither PhH nor Ph_2 could be found in any of the runs. Concentrations corresponding to 1% yields would have been detected. [c] Normalized to 100%. Total recovery was 98–100% except where noted. [d] 1.1 mol/mol of $Ph_2I^+Cl^-$. [e] 3.2 mol/mol of $Ph_2I^+Cl^-$. [f] Reaction time was 4 hr. [g] 3.1 mol/mol of $Ph_2I^+Cl^-$. [h] Solvent was not deaerated.

the proposed mechanism was derived largely from kinetic studies,[15] polarographic data,[3] and product analysis of the copper-catalyzed decomposition of unsymmetrically substituted iodonium salts.[4a,8] A recently suggested mechanism involves heterolytic carbon–iodine bond cleavages.[16] However, this mechanism seems to be precluded by the insensitivity of the carbon–iodine bond cleavage to the polar nature of the substituents in unsymmetrical iodonium salts.[4,8]

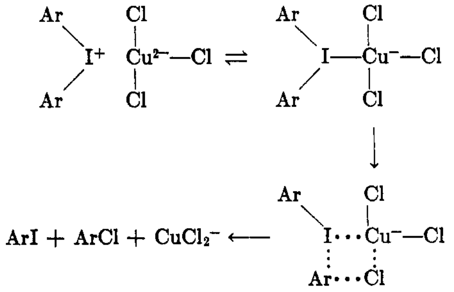
We have reinvestigated the copper(I) chloride catalyzed decomposition of 4-nitro- and 4-methoxydiphenyliodonium chloride and found the cleavage ratio C_6H_5–I/RC_6H_5–I to be 1.5 in both cases. This is in close agreement with previously reported data[4a,8] and with the ratio determined for the titanium(II) catalyzed reaction. However, copper-catalyzed reactions of diphenyliodonium chloride in water, methanol and acetone did not yield any benzene or biphenyl, the expected products from reactions involving phenyl free radical intermediates (Table III). Moreover, neither arylated products nor polymers were detected when reactions were carried out in the presence of α,β-unsaturated substrates of types used in Meerwein arylations (acrylonitrile was most intensively studied).[17] The absence of free-radical intermediates have been substantiated only for cases involving ligand transfer of chlorine, iodine and water. These results are in strong contrast to those obtained from the copper-catalyzed reactions of diazonium salts[14] and with those reactions of iodonium salts[4a,5] which proceed *via* electron transfer. In each of these cases the existence of free radical intermediates has been clearly demonstrated.

The differences in products in the decomposition of diphenyliodonium chloride catalyzed with copper(I) and with titanium(III) point clearly to two different reaction paths. While a mechanism involving initial electron transfer to the iodonium ion best explains the products of the titanium(III)-catalyzed reaction, an alternative reaction path, which does not involve the intermediacy of phenyl free radicals, seems to operate in the copper(I)-catalyzed reaction. A previously reported observation[4a] that copper(I) catalyzes the reaction of cyanide ion with the diphenyliodonium ion, even at high cyanide concentrations, also seems to rule out an electron-transfer step as the oxidation potential of $Cu(CN)_2^-$ is highly negative ($E° = -1.12$ V).[18] Further, the faster reactions of the diphenyliodonium ion with copper(I) complexes than with more strongly reducing complexes of other metals suggests a different mechanism for the copper(I)-catalyzed reaction. For example, at 65° under identical conditions the decomposition of diphenyliodonium chloride was complete in less than 0.5 hr in the presence of copper(I) chloride and in more than 8 hr in the presence of titanium(III) chloride; for the reaction to proceed to completion in 1 hr in the presence of chromium(II) chloride, a temperature over 90° was necessary.

A modification of the previously proposed mechanism is therefore put forward for the copper(I) chloride-catalyzed decomposition of diaryliodonium salts: complex formation between copper(I) and the iodonium cation possibly involving donation of the 5s electrons of iodine to the empty 4p or 4d orbitals of copper with back donation from the filled 3d orbitals of copper to the empty 5d or 4f orbitals of iodine; subsequent decomposition of the complex *via* a four-center concerted process in which there is no net change in the oxidation state of copper. (Analogous four-center processes have been proposed for reactions of aryl halides with copper(I) chloride.[19])

In Scheme I the initial copper(I) species may be $CuCl_2^-$ or $CuCl_3^{2-}$, these being the predominant species

SCHEME I



---

[15] F. M. Beringer, E. M. Gindler, M. Rapoport, and R. J. Taylor, *J. Amer. Chem. Soc.*, **81**, 352 (1956).

[16] O. A. Chaltykyan, "Copper-Catalyzed Reactions," Consultants Bureau, New York, N. Y., p 60.

[17] Meerwein and coworkers have reported the arylation of several α,β-unsaturated substrates using diphenyliodonium iodide under the conditions of the Meerwein reaction but experimental details were not given: H. Meerwein, E. Buchner, and K. van Emster, *J. Prakt. Chem.*, **152**, 237 (1939).

[18] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice Hall, Inc., Englewood Cliffs, N. J., 1952.

[19] R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.* (London), **19**, 95 (1965).

present in aqueous solutions under the reaction conditions,[20] or solvated neutral species which might predominate in methanol and acetone.[19] In aqueous solutions a copper-bound water molecule may also undergo ligand transfer resulting in the formation of phenol.[7c] However, in acetone and methanol the only products are iodobenzene and chlorobenzene, thus indicating exclusive ligand transfer of chloride. In agreement with other workers,[7] chloride was found to undergo ligand transfer more effectively than water. Nitrate[7c,14b] and sulfate[7a] are not involved in ligand transfer reactions. High ratios of copper(II) sulfate or nitrate to copper(I) chloride increase yields of phenol, probably because competition for chloride ion results in more highly solvated copper(I) species in this system. While acid has no appreciable effect on the rate of hydrolysis,[8] increased chloride ion concentration completely eliminates phenol production (Table III).

In summary of this last point, while present data cannot give the exact structure of the proposed complex of the diphenyliodonium ion with a di- or trichlorocuprate(I) ion and thus the possibility exists of structures different from that suggested above, the experimental observations strongly indicate a concerted reaction mode without free aryl intermediates.

Experimental Section

Starting Materials. Reagents.—All reagents were Fisher Certified Reagents except as noted. Iodobenzene, bromobenzene and chlorobenzene were distilled. Acrylonitrile (Eastman) was distilled and stored in the dark. Diphenylamine sulfonate (0.005 *M*) was obtained from the G. Fredrich Smith Chemical Co., Ohio.

Solvents.—Solvents for recrystallizations and reactions were deionized water, methanol (Electrograde, Nitine Inc.) and acetone (Fisher Certified Reagent, distilled from potassium carbonate).

Iodonium Salts.—4-Nitro- and 4-methoxydiphenyliodonium chloride were prepared by known procedures.[21,22] Diphenyliodonium chloride was prepared by a variation worked out by Doptoglon, of a previously reported procedure.[22,23] Diphenyliodonium iodide[24] is easily prepared by adding potassium iodide to an aqueous solution of diphenyliodonium chloride.

Copper Solutions.—Copper(I) solution was prepared by dissolving cuprous chloride in a deaerated 1 *M* lithium chloride solution in water. The clear colorless solution, stored in the dark in a bottle stoppered with a rubber septum, was titrated periodically. Concentration of copper(I) (0.0720 *M*) was found to be invariant. Aliquots were removed *via* syringe while argon was being bubbled through the solution and were used for all copper(I)-catalyzed reactions in aqueous solvents. For reactions in nonaqueous solvents copper(I) solution were made up as needed in deaerated 1 *M* lithium chloride solutions of methanol or acetone. Copper(II) solutions were made up as needed by dissolving the cupric salt in a minimum of solvent. For reactions in which both copper species were used, the copper(I) and copper(II) solutions were mixed before their addition to the reaction mixture.

Titanous Chloride.—Commercially available 20% aqueous titanous chloride (Fisher) was used. Aliquots were removed as described above. Solutions were titrated for titanium(III) before use.

Chromous Chloride.—Solutions of 0.4 *M* chromous chloride in 0.4 *M* hydrochloric acid were prepared as previously reported[12] by reduction of an acidified potassium dichromate solution with excess 30% hydrogen peroxide, and the resulting chromic chloride was in turn reduced to chromous chloride with zinc amalgam (1% mercury). The solution was stored over zinc amalgam in a 2-l. three-necked flask fitted with a gas inlet for argon, a mercury seal and a stopcock fitted with a rubber septum through which aliquots were removed *via* syringe. Solutions showed signs of decomposition after 1 week due to gradual reduction of hydrogen ion by zinc; this finally raised the pH to such a value that hydrolytic precipitation of the chromous ion occurred.[12] Aliquots were titrated before use.

Analysis for Copper(I), Titanium(III), and Chromium(II) Species.—Copper(I), titanium(III) and chromium(II) were analyzed according to procedures described by Kolthoff and Dandell.[25] Solutions of these species were added to an excess of deaerated, acidified solution of ferric alum. The resulting ferrous species was titrated with standard potassium dichromate solution using diphenylamine sulfonate indicator. All determinations were repeated and agreed to within 3%.

Catalyzed Decomposition and Chemical Reduction of Diaryliodonium Salts.—A generalized procedure is described below. Product yields, reaction time and temperature, and ratios of moles of reagent to moles of $-I^{+}-$ are listed in Tables I–III.

Unless otherwise stated, all reactions were run in an inert atmosphere in a three-necked, 1-l. flask fitted with a condenser and an addition funnel. Argon, initially passed through a chromous chloride solution to remove oxygen, was dispersed through the solvent (200 ml), magnetically stirred at the temperature of the reaction, and was swept through the reaction system for 1.5 hr. Iodonium salt (30 mmol) was then added and argon was bubbled through for an additional 0.5 hr. Reactions were protected from the atmosphere by a mercury seal attached to the upper end of the condenser. Solutions of catalyst or reducing agent were admitted dropwise over a period of 10 min, the dropping funnel having been charged with reagent by means of a syringe through a rubber septum.

After the indicated time the reaction mixture was allowed to cool, acidified with hydrochloric acid (to prevent loss of possible phenols) and extracted five times with 40-ml portions of methylene chloride. When solvents were methanol or acetone, 1 l. of water was added before extraction. The methylene chloride solution was dried over magnesium sulfate, filtered and analyzed by vapor phase chromatography (vpc).

Gas Chromatographic Analysis.—Organic extracts in methylene chloride solutions were analyzed by vpc (Aerograph Model No. 1520A) on a 6 ft, 5% SE-30 column (on Chromosorb G A/W DMCS). The temperature was programmed: 2 min at 75°, then 4°/min to 250° with an initial helium flow rate of 50 ml/min. Bromobenzene was used as internal standard, and the thermal conductivities of all products were calibrated *vs.* bromobenzene. For product analysis of reactions of 4-nitro- and 4-methoxydiphenyliodonium chloride, biphenyl was used as the internal standard after preliminary investigations showed biphenyl not to be a product of these reactions. Thermal conductivities of all products were calibrated *vs.* biphenyl in these cases.

The yield of iodobenzene was used as a measure of the extent of reaction. This was occasionally checked by recovering unreacted iodonium salt, if any, as the iodide. These procedures agree to within 2% of each other. None of the reagents was found to react with iodobenzene or chlorobenzene under the conditions of the reaction.

Attempted Meerwein-Type Arylations.—Organic products from these reactions were extracted as previously described. In preliminary runs the methylene chloride solution was evaporated, the high-boiling residues were fractionally distilled at reduced pressure. Products were identified by vpc. In no case were products such as α-chlorohydrocinnamonitrile [bp 137–140° (15 mm)] arising from the arylation of acrylonitrile found.[26]

Deaerated substances were usually added to the reaction mixture prior to addition of catalyst. Alternative addition of a solution containing both substrate and catalyst made no difference in product distribution.

Reaction of Diphenyliodonium Chloride with Titanous Chloride in the Presence of Acrylonitrile.—Diphenyliodonium chloride

---

[20] G. Bodlaender and O. Strobeck, *Z. Inorg. Chem.*, **31**, 458 (1902); N. Szabo and Z. Szabo, *Z. Physik. Chem.*, **A166**, 228 (1933); R. Vesten, A. Somersalo, and B. Mueller, *Acta Chem. Scand.*, **7**, 745 (1953); T. Hurlen, *ibid.*, **16**, 279 (1962).

[21] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillian, G. Masullo, M. Mausner, and E. Sommer, *J. Amer. Chem. Soc.*, **81**, 342 (1959).

[22] F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *ibid.*, **75**, 2705 (1953).

[23] F. M. Beringer and D. D. Doptoglon, unpublished results.

[24] F. M. Beringer and E. M. Gindler, "Organic Compounds of Polyvalent Iodine;" Chilean Iodine Educational Bureau, Inc., New York, N. Y., 1956.

[25] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 1st ed, The Macmillian Co., New York, N. Y., 1947, p 596.

[26] C. G. Koelsch, *J. Amer. Chem. Soc.*, **65**, 57 (1943).

reacted with titanous chloride in the presence of acrylonitrile to yield a white solid which began to appear after 20 min of reaction. After 8 hr at 80° titanous chloride was completely consumed, and 47% of the iodonium salt had reacted. A control reaction under identical conditions, but without iodonium salt, showed no change after 8 hr. The solid was collected, washed and triturated in turn with water, methanol and ether, yielding 5.0 g (63% based on starting acrylonitrile) of polyacrylonitrile. The polymer was dissolved in a minimum of dimethylformamide at 80–90°, and the solution was filtered hot through Celite. Water was slowly added to the cooled solution until no more precipitation occurred. The collected solid was dried to yield 3.0 g of polyacrylonitrile, mp 250° dec (lit.[13] 250–310° dec).

Identification was made from solubility characteristics and infrared and nmr spectra. The polymer was found to be insoluble in water, alcohols, acetone, ethylacetate, ether, methylene chloride and pentane but was soluble in dimethylformamide.[13] An infrared spectrum (potassium bromide pellet) exhibited strong peaks at 2230 (–CN), 1450 (CH, CH_2) and 1050 cm^{-1} (C–C skeletal).[13] An nmr spectrum (on a Varian A-60 spectrometer) of a solution in deuterated dimethyl sulfoxide exhibited broad signals at τ 7.9 and 6.8 and a very weak signal at 2.7.

Registry No.—Diphenyliodonium chloride, 1483-72-3; titanous chloride, 7705-07-9; chromous chloride, 10049-05-5.

Deuterium Isotope Effect upon a Bimolecular Dehydrochlorination of *t*-Butyl Chloride in Acetonitrile

DENNIS N. KEVILL AND JAMES E. DORSEY

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received August 26, 1968

We have extended our recent study of the secondary deuterium isotope effect upon the unimolecular dehydrochlorination of *t*-butyl chloride in acetonitrile[1] to a study of the deuterium isotope effect under conditions for bimolecular reaction in this solvent. It is known that bimolecular reactions of tertiary halides in dipolar aprotic solvents frequently show a small amount of substitution reaction accompanying dehydrohalogenation[2,3] and complications of this type have been avoided by use of chloride ion as the reagent to promote the bimolecular dehydrochlorination. Chloride ion in acetonitrile is quite efficient in this capacity[4] and, with this reagent, any substitution reaction will be symmetrical. The dehydrochlorination of *t*-butyl chloride is subject to marked reversal and, in the absence of reagents which remove hydrogen chloride, the reaction in aprotic solvents comes to an early equilibrium.[5] In the unimolecular dehydrochlorination,[1] added pyridine reacted with the hydrogen chloride to form pyridinium chloride[6] and prevent complications due to movement toward an equilibrium. In the presence of chloride ion, hydrogen chloride is effectively coordinated to give the hydrogen dichloride anion[7] and pyridine can be omitted.

A serious complication to the kinetic pattern is that the unimolecular reaction will be subject to a positive salt effect upon addition of tetraethylammonium chloride and the dehydrochlorination rate increase will consist of two components—one due to the superimposed bimolecular reaction and one due to a positive salt effect upon the underlying unimolecular reaction. In order to analyze the kinetics of the bimolecular reaction, we have attempted to arrive at the magnitude of salt effects upon the unimolecular reaction by assessing the rate increase upon addition of identical concentrations of tetraethylammonium perchlorate—a salt containing an anion which, relative to chloride ion, is ineffective in promoting bimolecular dehydrohalogenation in acetonitrile.[8] Perchlorate ion does not coordinate with hydrogen chloride and our studies of the effect of added tetraethylammonium perchlorate were carried out in the presence of pyridine (Table I).

Our kinetic results can be analyzed provided that we make the assumption that the salt effects upon the unimolecular reaction are identical (or, at least, very nearly so) for additions of either tetraethylammonium chloride or tetraethylammonium perchlorate (Table II).

The deuterium isotope effect (k_2^H/k_2^D) is 3.81 ± 0.21. The magnitude of this effect has important implications with respect to the mechanism of bimolecular, merged substitution and elimination which was given a detailed description several years ago,[4] and which recently appears to have gained wider,[9,10] but not universal,[11,12] acceptance. In assessing the extent of carbon–hydrogen bond breaking, and interpreting in terms of a mechanism in which carbon–chlorine heterolysis is running ahead of carbon–hydrogen heterolysis, we are on a scale of roughly 2.6:6 and not, as in most previous investigations, of roughly 1:6. With this in mind, the value of 3.8 is comparable with the values of between 2 and 3 observed for halide ion promoted elimination from tertiary α-halogenated ketones in acetonitrile.[13]

Under the same conditions of temperature and solvent, the deuterium isotope effect is significantly higher than the value of 2.62 ± 0.02 observed for E1 reaction.[1] This is consistent with a loose intermediate or transition state (approaching an ion triplet) and incorporating a moderate weakening of a carbon–hydrogen bond in the transition state of the rate-determining step.[13] If a transition state was involved which featured only SN2 character superimposed upon a E1-type process, then one might expect, related to the extent that the positive charge on the α carbon was reduced, an isotope effect for the bimolecular reaction diminished below that observed for the E1 reaction.

---

[1] D. N. Kevill and J. E. Dorsey, *Chem. Ind.* (London), 2174 (1967).

[2] D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **28**, 567 (1963).

[3] D. Cook and A. J. Parker, *J. Chem. Soc., B*, 142 (1968).

[4] D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 252 (1961); *J. Amer. Chem. Soc.*, **83**, 3812, 3815 (1961).

[5] Y. Pocker, *J. Chem. Soc.*, 1292 (1960).

[6] E. Gelles, E. D. Hughes, and C. K. Ingold, *ibid.*, 2918 (1954).

[7] Y. Pocker, *ibid.*, 240 (1958).

[8] G. A. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).

[9] G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc., B*, 425 (1967).

[10] A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

[11] D. J. McLennan, *J. Chem. Soc., B*, 705 (1966).

[12] J. F. Bunnett and E. Bacciochi, *J. Org. Chem.*, **32**, 11 (1967).

[13] D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Amer. Chem. Soc.*, **88**, 4489 (1966).