available the most reliable value of the entropy of cyanogen is the calorimetric one, 57.64 cal. deg.$^{-1}$ mole^{-1} at 298.1°K. and one atmosphere.

This value does not include the nuclear spin entropy.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

The Decomposition of Some Iodonium Salts. Reactions with Mercury, Tellurium and Antimony

BY R. B. SANDIN, F. T. McCLURE[1] AND F. IRWIN[2]

Recently H. J. Lucas and co-workers[3] have shown that di-o-tolyliodonium iodide decomposes at 155° into o-iodotoluene, uncontaminated by any isomeric product. They suggest that the mechanism involves a decomposition which proceeds through an intermediate, positively charged o-tolyl ion in which the positive charge is carried by a carbon atom. The positive o-tolyl ion then combines with the negative iodide ion of the iodonium salt to form a molecule of o-iodotoluene.

This plausible mechanism fits in with the fact that it is now known definitely that the I–I bond in diphenyliodonium iodide is an ionic, not a covalent, bond.[4] However, the authors of this paper became interested in the possibility that the decomposition of iodonium salts might, to some extent at least, be a non-ionic one and might proceed through the intermediate formation of free radicals. A non-ionic mechanism might explain the fact that the decomposition temperature of an iodonium salt depends upon the nature of the anion as well as the cation. For example, di-o-tolyliodonium bromide decomposes at 178°, the iodide at 155° and the sulfide at room temperature. If the decomposition involved only the positive ion, it is conceivable that the decomposition temperatures would lie closer together. Keeping the positive ion the same, we find roughly that the decomposition temperature of an iodonium salt varies directly with the electronegativity of the negative ion. Again, it is in a reaction such as this where one might look for the formation of free radicals. The latter are likely to be formed from those molecules which readily tend to undergo thermal self-decomposition at comparatively low temperatures (e. g., explosives, endothermic compounds, etc.). Finally, the re-

cent work of Waters[5] and co-workers on the decomposition reactions of the aromatic diazo compounds gave the present workers some hope in the idea that iodonium salts might behave similarly to diazonium salts.[6] Waters has shown that the diazonium chlorides can decompose by a non-ionic mechanism $(PhN_2)^+Cl^- \longrightarrow Ph\text{-}N{=}N\text{-}Cl \longrightarrow Ph\cdot + N_2 + \cdot Cl$, giving transient free neutral aryl radicals which are identical in chemical behavior with the neutral alkyl radicals[7] which have been studied in the gaseous phase.

The authors of this paper have carried out the decomposition of diphenyliodonium chloride and sulfide and di-p-tolyliodonium chloride in the presence of mercury, tellurium and antimony. In all cases, reactions have occurred which suggest the intermediate formation of free aryl radicals. Similarly, Waters[5] has found that benzenediazonium chloride decomposes under acetone kept neutral with chalk, in such a way that mercury, tellurium and antimony are attacked. Waters concludes that in the reaction mixture the free phenyl radical has a transient existence and that the phenyl radical is formed by thermal or photochemical decompositions of organic molecules in the liquid phase as well as in the gaseous phase.[8]

In view of the results obtained, it seems especially tempting to assume that in the decomposition of an iodonium salt, part of it at least can decompose by way of a non-ionic mechanism. The assumption is made that in the iodonium salt the

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(3) H. J. Lucas, E. R. Kennedy and C. A. Wilmot, THIS JOURNAL, **58**, 157 (1936).

(4) Medlin, ibid., **57**, 1026 (1935).

(5) (a) Waters, J. Chem. Soc., 1077 (1938); (b) Makin and Waters, ibid., 843 (1938); (c) Waters, ibid., 113. 2007, 2014 (1937). For a thorough review on free radicals in solution, see Hey and Waters, Chem. Rev., **21**, 169 (1937).

(6) There is a fundamental relationship between diazonium salts and iodonium salts in that the former are quaternary ammonium salts (i. e., fully substituted ammonium salts) and the latter are fully substituted derivatives of the hypothetical $(H_2I)^+X$.

(7) For an excellent treatise see F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

(8) (a) Zartman and Adkins, THIS JOURNAL, **54**, 3398 (1932); (b) Dull and Simons, ibid., **55**, 3898, 4328 (1933); (c) Glazebrook and Pearson, J. Chem. Soc., 589 (1939).

central iodine atom is able, by expanding its valence shell, to act as an acceptor for the chloride or sulfide ion. Subsequent transformations of this complex result from the tendency of the central atom to revert to an octet. The following is suggested as a probable course of the reaction: $(C_6H_5)_2I^+ + Cl^- \longrightarrow (C_6H_5)_2I \longleftarrow Cl \longrightarrow C_6H_5I + C_6H_5\cdot + \cdot Cl$. The expanded valence shell has been used to explain the marked difference in the mode of decomposition of the quaternary ammonium bases from the corresponding phosphonium bases. It also has been used in connection with the unusual reactions of, and formation of, the 2- and 3-covalent iodine compounds.[9]

The above conclusions of the authors are based largely upon the analogy between the reactions of iodonium compounds and the reactions of diazonium compounds studied by Waters and co-workers. Dr. H. J. Lucas of the California Institute of Technology has kindly drawn attention to the important role played by the metal in the decomposition reactions. He suggests the possibility of an intermediate, undissociated complex which decomposes at a lower temperature than the salt would otherwise. Such a reaction mechanism would not necessarily involve the formation of free radicals. On this basis also, the decomposition with and without a metal would not necessarily have to proceed via similar mechanisms.

Experimental Part

Preparation of Compounds.—Diphenyliodonium chloride and di-p-tolyliodonium chloride were prepared readily by a standard procedure.[3] It seems impossible to isolate an iodonium sulfide compound. Diphenyliodonium hydroxide, for example, when treated with sodium sulfide, produces a bright yellow precipitate (evidently the sulfide) which quickly decomposes into phenyl iodide and phenyl sulfide.[10] For that reason, in any of the decomposition reactions involving an iodonium sulfide salt, a more stable salt such as the chloride was mixed with sodium sulfide, or aqueous hydrogen sulfide, and to this mixture the necessary element such as mercury was added.

Diphenyltellurium dibromide, m. p. 200°, was made according to Krafft and Lyons.[11]

Triphenylstibinic sulfide, m. p. 119–120°, was made from triphenylstibinic chloride according to the procedure of Kaufmann.[12]

Reaction with Mercury.—Diphenyliodonium chloride (3.0 g.) was dissolved in 150 cc. of boiling n-propyl alcohol.

(9) See discussion by Johnson in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1610.

(10) Hartmann and Meyer, *Ber.*, **27**, 502 (1894).

(11) Krafft and Lyons, *ibid.*, **27**, 1769 (1894).

(12) Kaufmann, *ibid.*, **41**, 2762 (1908); Christiansen, "Organic Derivatives of Antimony," The Chemical Catalog Co., Inc., New York, N. Y., 1925, p. 172.

To this was added about 2.0 cc. of mercury and the mixture was refluxed for about five hours. While the mixture was still hot it was filtered and, on cooling the filtrate, pure phenylmercuric chloride, m. p. 250°, crystallized out. The yield was 1.25 g. The same procedure carried out with the addition of finely divided calcium carbonate gave identical results. In the same manner, di-p-tolyliodonium chloride gave p-tolylmercuric chloride, m. p. 230°.

Changing the solvent from propyl alcohol to water did not seem to have any appreciable effect on the results. This seems peculiar, since one would expect a solvent such as water to favor an ionic decomposition. Waters[5] has found that the non-ionic decomposition of diazonium salts occurs best in such solvents as acetone and ethyl acetate.

Reaction with Tellurium.—Diphenyliodonium chloride was refluxed in an n-propyl alcohol solution with finely divided tellurium. After several hours the unchanged tellurium was filtered off and the filtrate evaporated to a small volume. On the addition of bromine, yellow crystals of diphenyltellurium dibromide, m. p. 199–200°, crystallized out. These crystals, mixed with a sample of synthetic material, produced no depression of the melting point. When water was used as a solvent, only once, out of several attempts, was enough diphenyltellurium dibromide obtained for a melting point determination. These results might indicate that an ionic decomposition occurs in a highly polar solvent such as water. It was also observed that when water was used as the solvent, finely divided tellurium speeded up the decomposition of the iodonium salt.

When a mixture of diphenyliodonium chloride dissolved in water, tellurium, ether and aqueous hydrogen sulfide, was shaken up in a flask for about an hour at room temperature, diphenyltellurium was again formed. The diphenyltellurium dissolved in the ether layer and was isolated as the yellow dibromide.

Similar results to the above were obtained when di-p-tolyliodonium chloride was used instead of the phenyl compound. Di-p-tolyltellurium was isolated as the yellow dibromide, m. p. 203–204°.

When a mixture of diphenyliodonium chloride and finely divided tellurium was heated in the dry condition in a test-tube, diphenyltellurium dichloride, m. p. 158°, was formed. The tellurium had also the effect of lowering the decomposition temperature of the iodonium chloride.

Reaction with Antimony.—A solution of diphenyliodonium chloride in water was shaken up at room temperature with sodium sulfide, finely divided antimony and ether. The ether layer was separated, filtered and, on evaporating to dryness, beautiful crystals of triphenylstibinic sulfide, m. p. 119–120°, were left behind. They had a slight yellowish tinge and when mixed with a synthetic sample produced no depression of the melting point

Summary

1. Diphenyliodonium chloride and di-p-tolyliodonium chloride react with mercury in boiling n-propyl alcohol to produce phenyl and p-tolyl mercuric chloride. With tellurium they give diphenyltellurium and di-p-tolyltellurium. Di-

phenyliodonium sulfide decomposes at room temperature in the presence of tellurium and antimony to give diphenyltellurium and triphenylstibinic sulfide.

2. To account for these reactions, it is suggested that at least a part of the iodonium salt decomposes by way of a non-ionic mechanism.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Tyrosinase from the Wild Mushroom, *Lactarius Piperatus*

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Kubowitz[1,2] has shown that potato oxidase (tyrosinase) contains copper and that the activity of the oxidase toward catechol as the substrate is proportional to the metal content. After considerable purification a product was obtained which in the presence of acetone, at 0°, occurred in a globular form and contained 0.20% copper. Keilin and Mann[3] have also prepared a highly purified polyphenolase (*i. e.*, tyrosinase) from the common mushroom, *Psalliota campestris*, which had a copper content of 0.30% and an activity toward catechol proportional to the copper content.

The tyrosinase described in the present communication was prepared from the wild mushroom, *Lactarius piperatus*. Highly purified preparations from this source were found to contain 0.23% copper. The activity of these preparations toward catechol was also proportional to the copper content (see Fig. 1). The copper was
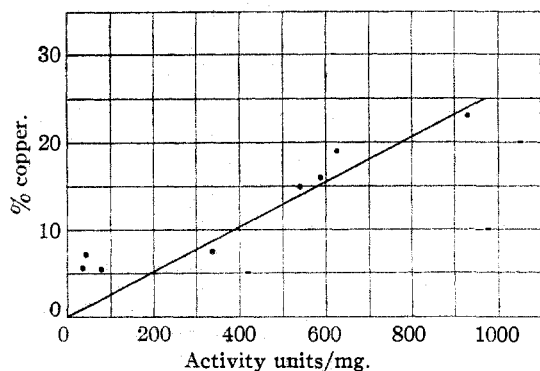

Fig. 1.

easily removed from the enzyme preparation by dilute acids just as Kubowitz noted in the case of the oxidase from potatoes. Contrary to the claims by Yakushiji[4] that the polyphenolase from

Lactarius piperatus contains a hematin residue; the data in the table clearly show that the iron can be removed completely by one adsorption to kaolin. Only in the case of the two crude preparations, nos. 1 and 2, was iron found to be present and then only in very small amounts. It therefore appears that iron was present only as an impurity in the crude preparations.

Keilin and Mann[3] found no relationship between the activities of their oxidase preparations, from *Psalliota campestris*, toward the two substrates, *p*-cresol and catechol, and were inclined to attribute the activity toward *p*-cresol as involving the presence of some other factor in the reaction mixture. Likewise Adams and Nelson[8] were able to vary, in the case of the oxidase from *Psalliota campestris*, the ratio between the activities toward these two substrates. On the other hand, the last-mentioned investigators were unable by similar procedures, such as the use of various adsorbing materials, to alter the ratio of these two activities in the case of the tyrosinase from *Lactarius piperatus*. Further attempts in the present study to vary this ratio by treating the enzyme solutions with lead acetate and with silver acetate also were unsuccessful. All the preparations examined showed about 10 cresolase units to 1 catecholase unit.

The quantity of copper corresponding to one unit of cresolase is given in the table for several preparations. The rather crude preparations 1, 2 and 3 contain an appreciable quantity of undialyzable copper, which was also noticed by Keilin and Mann[3] in their crude preparations from *Psalliota campestris*, and hence show a high copper value per cresolase unit. Preparations 4 to 8 have lost this extraneous copper and the copper per cresolase unit reaches a constant value of approximately 0.0027 γ. These preparations represent enzyme in which all of the copper seems to be in an active form.

(1) F. Kubowitz, *Biochem. Z.*, **292**, 221 (1937).
(2) F. Kubowitz, *ibid.*, **299**, 443 (1938).
(3) D. Keilin and T. Mann, *Proc. Roy. Soc.* (London), **125B**, 187 (1938).
(4) E. Yakushiji, *Acta Phytochim. Tokyo*, **10**, 63 (1937).