

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

The Decomposition of Some Iodonium Salts¹

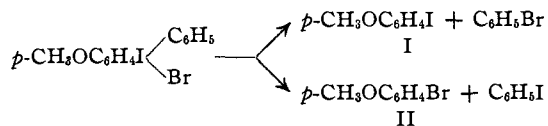
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Introduction

In a recent publication, H. J. Lucas and co-workers² have shown definitely that di-*o*-tolylidonium iodide decomposes at 155° into *o*-iodotoluene. A very plausible mechanism of the rearrangement put forward by these workers involves first the formation from the di-*o*-tolylidonium ion of equal amounts of *o*-iodotoluene and positive *o*-tolyl ion by the scission of a C-I bond, and second the combination of this ion with the negative iodide ion, to form a second molecule of *o*-iodotoluene.

In the above work the iodonium salt concerned is a symmetrical one from the standpoint of the two organic radicals. If the two organic radicals are different the situation is a little more complicated. The decomposition of an unsymmetrical iodonium salt should give two products if it is an iodide and four products if it is not an iodide. A search of the literature revealed the fact that relatively few salts of this type have been studied from the view point of rearrangement. Thiele and Umnoff³ have shown that the decomposition of dichlorovinylphenyliodonium bromide gives phenyl iodide and dichlorobromoethylene. They have also indicated that dichlorovinylchlorovinylidonium bromide yields chloriodoethylene and dichlorobromoethylene. However, these workers made no attempt to study the reaction quantitatively, nor did they establish definitely the nature of the end products.

The authors of this paper have prepared and carried out the thermal decomposition of phenyl-*p*-anisylidonium iodide, bromide and chloride. The decomposition of the bromide, taken as an example, may follow one or both of the reaction schemes indicated below.



Actually, it has been shown that at least 87%

(1) Abstracted in part from a thesis submitted by M. Kulka to the Graduate School of the University of Alberta for the degree of Master of Science.

(2) H. J. Lucas, E. R. Kennedy and C. A. Wilmot, *THIS JOURNAL*, **53**, 157 (1936).

(3) Thiele and Umnoff, *Ann.*, **369**, 147 (1909).

and possibly more of the decomposition follows the first reaction scheme. This is what one might predict from Kharasch's table of the relative electronegativity of organic radicals.⁴ The original positive ion evidently rearranges in such a way that the more electronegative radical (in this case the *p*-anisyl radical) remains attached to the iodine atom. Considered from this viewpoint, the results recorded by Thiele and Umnoff³ are what one might expect. Preliminary results on the rearrangement of other iodonium salts, being carried out in this Laboratory, seem to indicate that this is the general mode of decomposition. The reason why the phenyl and the *p*-anisyl radicals were used in this work was because, first of all, they were relatively far apart in Kharasch's table, and, second, the use of the latter radical lent itself to a quantitative procedure which is described in the experimental part of this paper.

Experimental Part

Preparation of Phenyl-*p*-anisylidonium Halides.—A method similar to that of Lucas and co-workers² was followed. A mixture of equimolar amounts of iodosobenzene and *p*-iodoxyanisole⁵ (11.0 g. and 13.3 g., respectively) with 0.5 g. of freshly precipitated moist silver oxide was ground in a mortar with about 10 cc. of chloroform.⁶ Water was added and the mixture allowed to stand for about a day. The water was then poured off into a flask and to it was added potassium bromide. A precipitate of the iodonium bromide was produced. More water was added to the mixture in the mortar and the grinding continued. This process was repeated until the aqueous extract gave no precipitate with potassium bromide. Sometimes five to six days were required for the reaction to go to completion. A 75% yield of the crude product was obtained. It crystallized from water in white needles.

Anal. Calcd. for C₁₃H₁₂OBrI: Br, 20.44. Found: Br, 20.30, 20.40.

By adding potassium chloride, instead of the bromide, to the aqueous extract, phenyl-*p*-anisylidonium chloride was produced. It separated in the form of white granular crystals from water.

Anal. Calcd. for C₁₃H₁₂OClI: Cl, 10.24. Found: Cl, 10.04.

(4) (a) Kharasch and Graffin, *THIS JOURNAL*, **47**, 1948 (1925); (b) Kharasch and Marker, *ibid.*, **48**, 3130 (1926); (c) Kharasch and Fleener, *ibid.*, **54**, 674 (1932).

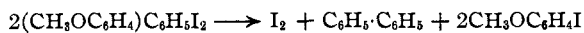
(5) Von A. Liebrecht, German Patent, 161,725, June 27, 1905.

(6) The authors have found that the use of a mixture of iodoxybenzene and *p*-iodoxyanisole gave no appreciable amount of iodonium compound.

A similar procedure was used in the preparation of phenyl-*p*-anisylidonium iodide. It was relatively insoluble in water, from which it had a tendency to crystallize in pale yellow needles. One preparation gave a white product, but this, on standing exposed to light, turned yellow.

Anal. Calcd. for $C_{13}H_{12}OI_2$: I, 28.98. Found: I, 28.92, 28.80.

Decomposition of the Iodonium Salts.—The decomposition was effected by immersing a large Pyrex test-tube containing about 5 g. of the salt in a glycerol-bath heated to the required temperature. The test-tube was provided with an ordinary piece of glass tubing to act as a reflux tube. The iodide decomposed at 175°, the bromide at 180°, and the chloride at 181°. In the case of the bromide and the chloride, the amount of free iodine liberated as a result of the decomposition was negligible, compared with the total amount present. When the iodide underwent decomposition, 4.2% of the total iodine was liberated as such. It is believed that the greater portion of this free iodine is due to the iodide ion acting as a reducing agent. This secondary reaction presumably proceeds as follows



Qualitative Identification of the Reaction Products.—The reaction product from each salt was distilled fractionally and in each case the higher boiling fraction (above 200°) solidified on cooling, and upon a single crystallization from alcohol proved to be pure *p*-iodoanisole, m. p. 51–52°. The lower boiling fraction (below 200°) in each case was refluxed for several hours with acetic anhydride and concentrated hydriodic acid. It was then made alkaline and steam distilled. From the steam distillate there was isolated phenyl iodide, phenyl bromide or phenyl chloride, corresponding originally to the iodonium iodide, bromide or chloride. These compounds were identified by micro boiling points and also, in the case of the phenyl bromide, by analysis.

Quantitative Examination of the Reaction Products.—A quantitative estimation of the *p*-iodoanisole in each of the reaction products was carried out by refluxing for a period of ten hours a definite amount of the reaction product (about 1 g.) with 8 g. of stannous chloride, 15 cc. of 40% hydrobromic acid, 15 cc. of glacial acetic acid and 5 cc. of water. The mixture was then made alkaline with sodium bicarbonate and steam distilled. The residue was made acid with sulfuric acid, and the iodine liberated by the addition of ferric chloride, and a second steam distillation was carried out. The iodine in the distillate was determined by a thiosulfate titration. Pure *p*-iodoanisole under these conditions was found to give up 95% of its total iodine, whereas in the case of phenyl iodide the amount of iodine liberated was negligible. On this basis the reaction product from the iodonium bromide gave evidence that at least 87% of the total iodine was present as *p*-iodoanisole. The iodonium chloride showed at least 88% and the iodonium iodide 96%. In the latter case the free iodine already present was considered as having come from the iodide ion.

In the above procedure, when refluxing with stannous chloride, it is essential that glass beads be used to prevent bumping. It is also essential that the ten-hour period of refluxing be not interrupted.

Summary

Phenyl-*p*-anisylidonium iodide, bromide, and chloride have been prepared. The latter two salts on thermal decomposition have been shown to decompose mainly in such a way that the more electronegative radical (*p*-anisyl radical), based on Kharasch's table, remains attached to the iodine atom.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Dissociation Pressures of Potassium Deuteride and Potassium Hydride¹

BY EDITH FORD SOLLERS² AND J. L. CRENSHAW

Introduction

Almost all of the numerous comparative studies of compounds containing ordinary and heavy hydrogen have been made on compounds in which the hydrogen was combined with non-metals. Relatively few comparisons of the salt-like metallic hydrides and deuterides, in which the hydrogen is in the form of anions,³ have been made.

(1) This article is based on the dissertation presented to the Faculty of the Graduate School of Bryn Mawr College by Edith Ford Sollers in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The complete dissertation is on file in the Bryn Mawr College library.

(2) Alice Freeman Palmer Fellow of Wellesley College.

(3) See Peters, *Z. anorg. allgem. Chem.*, **131**, 140 (1923), where references to previous work are given.

A study of the dissociation pressures of these compounds seemed to be of interest from a theoretical point of view and also the results might lead to a new method for the separation of the two hydrogen isotopes.

The dissociation pressures of the hydrides of the alkali and alkaline earth metals have been measured by many investigators but except for a brief statement by Tronstad⁴ about the lithium compounds, no data on the dissociation pressures of the deuterides of these metals have been published. The potassium compounds were chosen

(4) Tronstad, "Nordiska (19 Skandinaviska) Naturforskarmotd 1 Helsingford Den. 11–15 Augusti 1936," p. 381.