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The Gross Mechanism of the Victor Meyer and Hartmann Reaction[1]

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Iodosobenzene-I^{131} and iodoxybenzene have been allowed to react in the presence of alkali to yield diphenyliodonium iodate. It has been shown that the radioactivity of the product occurs almost exclusively in the diphenyliodonium ion. A mechanism which is consistent with this and other previous observations is suggested for the reaction.

The reaction between an aryliodoso compound (I) and an aryliodoxy compound (II) in the presence of alkali to yield a diaryliodonium iodate (III) has been termed the Victor Meyer and Hartmann reaction.[2] A mechanism involving a cyclic complex has been proposed for it,[2a] which, however, does not account for the alkali catalysis observed.

In an effort to obtain some evidence bearing on the question of the mechanism, diphenyliodonium iodate has been prepared by the reaction of iodoxybenzene and iodosobenzene-I^{131}.

$$\underset{\text{I}}{\text{Ar-IO}} + \underset{\text{II}}{\text{Ar-IO}_2} \xrightarrow{\text{OH}^-} \underset{\text{III}}{\text{Ar}_2\text{I}^+ + \text{IO}_3^-}$$

The iodosobenzene-I^{131} was prepared by a standard procedure.[3] The diphenyliodonium iodate was analyzed by precipitation of the diphenyliodonium ion from aqueous solution as the bromide, followed by precipitation of the iodate as the barium salt. The purified samples were mounted and counted, utilizing the γ-radiation of the I^{131} only, in order to avoid complications from self-absorption and back-scattering. The results are shown in Table I.

TABLE I

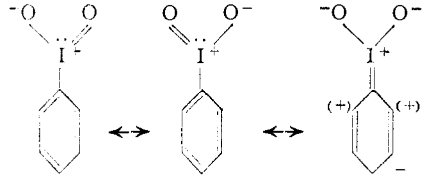
Substance	Wt. sample	Obsd. ct./min.[a]	ct./min. mg. 1
C_6H_5IO	0.0192	792	71 (single detn.)
$C_6H_5I^+Br$	.0279	1765	63 ± 1
	.0455	2874	
$Ba(IO_3)_2$	.1050	105	1 ± 1
	.0939	95	

[a] Corrected for background.

It can be seen that it is the iodine of the iodosobenzene which turns up in the diphenyliodonium ion, the iodine of the iodoxybenzene being oxidized to iodate. In view of these results, one may draw two conclusions: (1) there is no symmetrical intermediate involving both iodine atoms; (2) the isotope exchange reaction between iodosobenzene and iodoxybenzene is slow, compared to the rate of formation of the iodonium salt.

The specific activity of the diphenyliodonium bromide is slightly lower than that of the starting material. This may be explained by the previously observed formation of diphenyliodonium salts from iodoxybenzene alone in the presence of alkalies.[2a] The slight activity in the iodate fraction may arise from impurity, or by disproportionation of iodosobenzene to iodobenzene and iodoxybenzene followed by reaction of the iodoxybenzene-I^{131} so produced with more iodosobenzene.

Since the structures of the polyvalent organic iodine compounds are not yet very well understood, any proposals concerning the mechanism of this reaction must be highly speculative. Nitration of iodoxybenzene (probably in the form of its salt with sulfuric acid) leads practically exclusively to *m*-nitroiodoxybenzene.[2a] In view of this strong meta-directing influence, and by natural analogy to the nitro group, one is tempted to write resonance structures for iodoxybenzene such as IV, V and VI.



IV V VI

However, the simple valence bond picture of these forms with a double bond to the iodine requires the utilization of the iodine 5d orbitals. If the energy required for this electronic structure is comparatively large, then these forms will not contribute as much to the resonance hybrid as do the corresponding forms of nitrobenzene. The question of valence-shell expansion has been discussed fully by Sutton and co-workers.[4]

Accepting the current view of the mechanism of aromatic nucleophilic substitution reactions,[5] it is of interest to note that the reaction of azide ion with *p*-nitroiodoxybenzene gives *p*-nitrophenylazide, with nucleophilic displacement of the iodoxy group,

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission. While this paper was in process, the paper by J. B. Th. Aten and A. H. W. Aten, Jr., THIS JOURNAL, **74**, 2411 (1952), appeared in which were reported the results of experiments similar to ours. However since our work differs from theirs in point of experimental detail and interpretation, we are presenting it here.

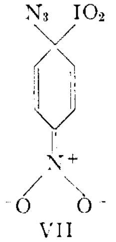
[2] (a) I. Masson, E. Race and F. E. Pounder, *J. Chem. Soc.*, 1669 (1935); (b) C. Hartmann and Victor Meyer, *Ber.*, **27**, 504 (1894).

[3] H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 331; *Org. Syntheses*, **22**, 69 (1942); H. J. Lucas, E. R. Kennedy and M. W. Formo, *ibid.*, **22**, 70 (1942).

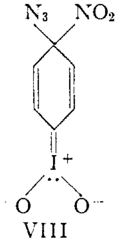
[4] L. E. Sutton, *Ann. Repts.*, **37**, 73 (1940); C. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945); Z. Z. Hugus, Jr., THIS JOURNAL, **74**, 1076 (1952), in which the use of 4f orbitals in iodine bonding is discussed.

[5] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 297 (1951).

rather than *p*-iodoxyphenylazide, with replacement of the nitro group.[6] A possible explanation is that the transition state for iodoxy replacement (VII) has a lower energy than that for nitro replacement (VIII) because of the energy required to form the C–I double bond.

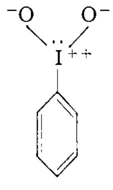


VII



VIII

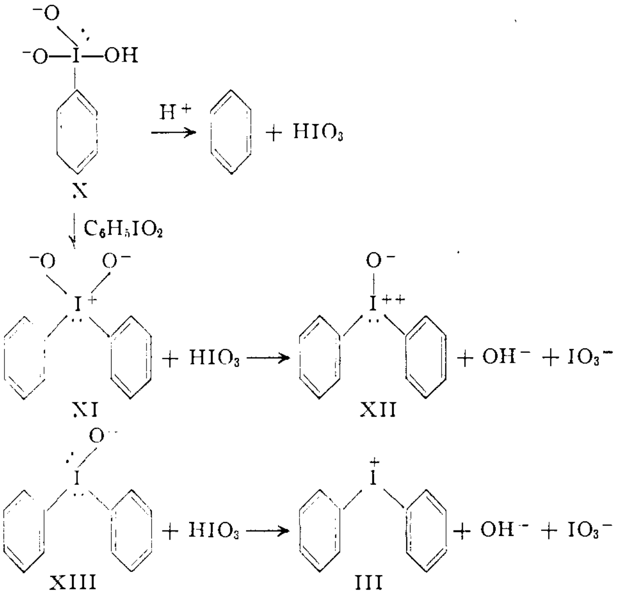
Thus the form which probably contributes the most to the structure of iodoxybenzene is that in which purely dative bonds are formed between the iodine and oxygen atoms (IX)



IX

On this basis the meta-orienting effect is explained mainly as an inductive effect.

Masson and co-workers suggest that the solubility of iodoxybenzene in alkali is due to a reversible addition of a hydroxyl group, to give an anion (X), with pK_a about 11. The formation of such an anion would again require utilization of the iodine 5d shell, and consequently would not be expected to be very stable. The C–I$^+$ bond could easily break at the demand of an approaching positive center in a concerted reaction giving a molecule of iodic acid and a phenide ion coördinated with the positive center. If the positive center were a proton, the product would be a hydrocarbon. This type of product has been observed.[7]



If the approaching positive center were the iodine atom of another molecule of iodoxybenzene, the product would be a new negative ion of structure XI, which itself would not be very stable but would pick up a proton, and ionize further to give the base XII. A compound corresponding in empirical formula to the acetate of this base has been isolated.[2a]

Finally, if the approaching positive center is the iodine atom of an iodoso group, the negative ion would have the structure XIII, which on hydrolysis would lead to the diphenyliodonium iodate product.

This, then, seems an attractive mechanism, inasmuch as it is compatible with the known facts. More information is needed concerning the structures and reactivities of the iodoso and iodoxy groups and it is intended to undertake further work in this direction.

Experimental

Iodosobenzene-I^{131}.—The sequence of reactions leading from aniline through iodobenzene and iodobenzene dichloride was carried out as described in reference 3, with the following modifications: 2.97 g. of potassium iodide containing approximately 0.4 mc. of radioactive iodine was added to the appropriate amount of diazotized aniline in the first step; the steam distilled product was dried by addition of 9 ml. of benzene, and distillation of the water–benzene azeotrope at atmospheric pressure. The iodobenzene-I^{131} was purified by distillation under reduced pressure through a 30-cm. Podbielniak column. The fraction collected boiled at 75–76° at 20 mm. As far as possible, all operations were carried out in an atmosphere of nitrogen and in a closed system vented only through Dry Ice and acetone-cooled traps.

Steps 2 and 3 were conducted essentially without departure from the directions in the literature.[3] The yield of iodosobenzene-I^{131} amounted to 0.70 g. and had a total activity (calculated) of 0.036 mc. The over-all chemical yield from potassium iodide was 20%.

Iodoxybenzene.—The compound was prepared by disproportionation of iodosobenzene, as described by Willgerodt.[8] The iodometric titer was 100 ± 2% of the theoretical.

Diphenyliodonium-I^{131} Iodate.—A 0.0192-g. sample of the iodosobenzene-I^{131} was reserved for counting. The rest was allowed to react with an excess of iodoxybenzene according to the directions of Lucas and Kennedy.[9] To the clear diphenyliodonium iodate solution obtained, 20 ml. of normal potassium bromide solution was added, precipitating white needles of diphenyliodonium bromide. These were filtered from the chilled solution, and a second 5-ml. portion of potassium bromide solution added to assure the completeness of the separation. To the clear filtrate was then added 20 ml. of saturated barium hydroxide solution, giving a white granular precipitate of barium iodate, which was filtered onto two weighed fritted glass counting disks. The diphenyliodonium bromide was recrystallized from hot water and filtered onto two similar weighed frits. The samples were dried, weighed and counted.

For counting, an end-window tube was used, having a window weight of 3.4 mg./cm.^{2} and a filling of 1 cm. pressure of ethanol plus 9 cm. pressure of argon. The tube was operated at 1300 v. The impulses were registered on an Instrument Development Laboratory scaling unit, model 162. The frits were placed in sample holders which could be reproducibly positioned under the tube. An aluminum sheet of weight 300 mg./cm.^{2} was placed between the sample and the tube to absorb the β radiation. Two records of at least 10,000 counts were taken of the high-activity samples, while two records of at least 1000 counts were taken of the low-activity samples. Background counting rate amounted to less than 10% of that of the low-activity sample.

UPTON, L. I., NEW YORK

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[6] D. Vorlander and H. David, *Ber.*, **70B**, 146 (1937).

[7] H. Lutgert, *ibid.*, **70B**, 151 (1937).

[8] C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigem Jod," Verlag von Ferdinand Enke, Stuttgart, 1914, p. 13, *Ber.*, **27**, 1826 (1894).

[9] H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **22**, 52 (1942).