311. *Stability against Interchange of the Iodine Atoms in Diphenyliodonium Iodide.*

By F. Juliusburger, B. Topley, and J. Weiss.

The ionic nature of crystalline diphenyliodonium iodide has recently been demonstrated by *X*-ray measurement of the distance between the iodine atoms in the solid (Medlin, *J. Amer. Chem. Soc.*, 1935, **57**, 1026).

Using radioactive sodium iodide prepared by neutron bombardment, we have examined by means of a Geiger counter the facility of interchange, in solution, of iodide ions with the two different iodine atoms in diphenyliodonium iodide.

The negatively charged atom naturally must interchange with sodium iodide in alcoholic and aqueous-alcoholic solution, and we have verified that this is so by crystallising diphenyliodonium iodide out of hot solutions to which activated sodium iodide had been added. The solid, after washing with ice-cold water, was strongly radioactive; after grinding with silver hydroxide and water, filtration of the diphenyliodonium hydroxide solution, and reprecipitation of the iodide by means of inactive sodium iodide, it was

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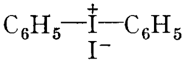
* This method was preferred to the less specific iodine titration of Ripper (*Monatsh.*, 1900, **21**, 1079).

inactive. Thus the interchange occurs with the negative iodine atom only. No interchange with the positive iodine atom could be detected after boiling for twenty minutes in alcohol and in 1 : 1 aqueous alcohol.

The decomposition of diphenyliodonium iodide into two molecules of iodobenzene has been quantitatively investigated by Fletcher and Hinshelwood (this vol., p. 596), who found that the decomposition takes place very much more rapidly in saturated solution in iodobenzene than in the solid.

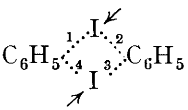
The mechanism of the decomposition in solution in iodobenzene is unknown, and there is no direct evidence as to the ionisation of the iodonium iodide in this solvent, but it seems probable that the solution contains ion pairs $(C_6H_5)_2I^+ . I^-$, and that the formation of iodobenzene results simply from the rearrangement of the bonds and charge distribution in these ion pairs.

Assuming that decomposition takes place through the break-up of an activated complex, it seemed to us an interesting possibility that exchange of the two iodine atoms might take place through a similar activated complex.

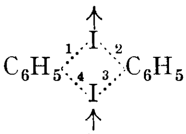


$\underset{I^-}{C_6H_5-\overset{+}{I}-C_6H_5}$

Ion pair.



Decomposition.



Exchange.

The formulæ with attached arrows represent activated complexes, in this case ion pairs with high potential energy. (The polar character of the normal ion pairs will now have given place to an approximately symmetrical distribution of electron density round the two iodine nuclei.) The internal kinetic energy of such a complex may be present in different ways : *e.g.*, if the direction of motion of the representative point on the potential energy "surface" (see Eyring, *J. Chem. Phys.*, 1935, **3**, 107) is such as to weaken bonds 2 and 4 whilst strengthening 3 and 1 as indicated in the central formula, then two bonds are formed and two are broken as the complex passes through the transition state; the final configuration is two molecules of iodobenzene. On the other hand, if the motion of the iodine nuclei is as indicated in the last formula, the original covalent bonds 1 and 2 will be broken and the new bonds 3 and 4 will be strengthened. Here again two bonds are broken and two formed, but the result is simply an interchange of the functions of the iodine atoms.

Actually, as is proved by the following experiment, no detectable exchange does take place even under conditions so extreme that considerable decomposition occurs before the reaction is stopped. We wish to say about this result only that it does not contradict the view that the activation energy is lower for decomposition than for exchange.

Diphenyliodonium iodide with the negative iodine active was prepared as above, and dried by washing with ether and slight heating. One part of this was put aside, and the remainder (*ca.* 1·5 g.) heated to 105° with 6 c.c. of iodobenzene for 5 minutes. From the velocity constants found by Fletcher and Hinshelwood (*loc. cit.*) we know that one quarter of the solid decomposes in the saturated solution under these conditions. The reaction mixture was rapidly cooled, and washed on to a filter with alcohol and water. The negative iodine atom was removed and replaced by inactive iodine as described above. After these operations the solid was completely inactive, whereas the original iodide was still strongly active, in spite of the radioactive decay during the time required for the chemical manipulation of the solutions.

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