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THE THERMAL DECOMPOSITION OF O-HYDROXY-DIAZONIUM COMPOUNDS

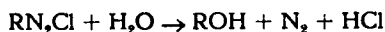
BY

J. DE JONGE, R. DIJKSTRA and P. B. BRAUN

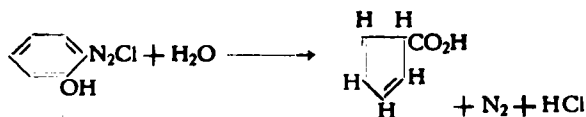
(N.V. Philips Gloeilampenfabrieken, Eindhoven, Nederland).

Experimental evidence has been found that the thermal decomposition of o-hydroxy-diazonium salts may be identical with the photo-decomposition.

The thermal as well as the photo-decomposition of diazonium compounds in water generally leads to the formation of the corresponding phenol:



Recently it had been found, however, that o-hydroxy-diazonium compounds of benzene or naphthalene show a very peculiar photo-decomposition^{1) 2)}. The benzene nucleus carrying the diazonium group is converted into a five-membered ring with the generation of a carboxyl group:



The presence of the carboxyl group in the photo-decomposition product could be demonstrated by the generation of CO₂ when the irradiated solution of the diazonium compound was heated²⁾.

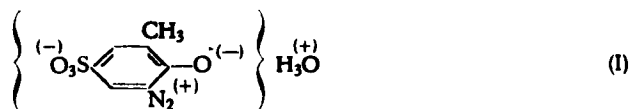
We can now submit experimental evidence that the *thermal* decomposition of o-hydroxy-diazonium salts in diluted solution may be identical with the photo-decomposition.

As o-hydroxy-diazonium salts are rather stable in solution, we effected the thermal decomposition by heating a solution to 100° C.

Thus from 1 mole of 1-hydroxy-2-diazonium-6-methylbenzene-4-sulphonic acid,

¹⁾ O. Süss, Ann. 556, 65, 85 (1944).

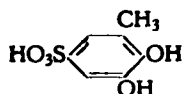
²⁾ J. de Jonge and R. Dijkstra, Rec. trav. chim. 67, 328 (1948).



we collected 0.8 mole of N_2 along with 0.8 mole of CO_2 .

The loss of CO_2 from the resulting thermal decomposition product may indicate the original formation of a carboxyl group, just as in the case of the photo-decomposition product.

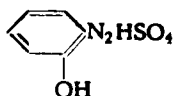
It goes without saying that a decomposition product like 1,2-dihydroxy-6-methylbenzene-sulphonic acid



would not produce CO_2 on heating at 100°C .

In the above experiment the diazonium salt was heated in a very dilute solution containing 0.015 mole per liter. This was to minimize the occurrence of inevitable secondary reactions, e.g. a coupling reaction of the still undecomposed diazonium salt with the decomposition product. Yet only 80 % of the theoretical amount of nitrogen was generated.

Even more secondary reactions occur in the thermal decomposition of *o*-hydroxy-benzenediazonium sulphate:



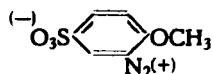
The heating of a solution resulted in the formation of some dark brown tarry solid. Yet there was (after 7 hours heating) a production of 0.33 mole carbon-dioxide for each mole diazonium compound originally present.

Probably the diazonium salt will in part be decomposed into cyclopentadiene-carboxylic acid and in part couple with the latter. Carbon dioxide will then be split off from the cyclopentadiene carboxylic acid, at least as far as this latter compound is not dimerised or polymerised before, for we found that already dimeric cyclopentadiene-carboxylic acid does not lose its carboxyl group at 100°C .

According to Crossley and co-workers the thermal decomposition of *o*-methoxy-benzene-diazonium chloride and other *o*-substituted derivatives of phenyl-diazonium chloride would occur with intermediate formation of a diazo oxide³⁾. Thus we may expect some carbon

³⁾ M. L. Crossley, R. H. Kienle, L. H. Benbrook and N. T. Woodberry, J. Am. Chem. Soc. 69, 1160 (1947).

dioxide in the gaseous products of the decomposition. In a qualitative experiment we actually did find a production of a small amount of carbon dioxide on heating a solution of 1-methoxy-2-diazonium-benzene-4-sulphonic acid for 3 hours at about 90° C:



Finally we may refer to an observation of *Vaughan and Phillips*⁴⁾. These authors studied the thermal decomposition of some nitro-benzene diazo oxides in the solid phase at a temperature of 50—80°. The gaseous decomposition products contained about 0.8 mole of nitrogen per mole diazo oxide, along with nearly 0.1 mole of carbon dioxide. This fact may be interpreted as a partial decarboxylation of nitro-cyclopentadiene carboxylic acid.

Experimental part.

132 mg (0.006 mole) 1-hydroxy-2-diazonium-6-methylbenzene-4-sulphonic acid (I) was dissolved in 400 ml water and placed in a 450 ml flask. This flask was fitted with a gas-inlet tube and a small water-cooled bulb-condenser. The top of the condenser was connected to an absorption tube filled with 0.1 N Ba(OH)₂.

After the apparatus had been cleared of carbon dioxide by means of a current of nitrogen the solution of the diazonium salt was heated for 2 hours in a bath of 102° C.

We found 95.0 and 92.5 mg of BaCO₃; this corresponds respectively to 80% and 78% of the theoretical amount of CO₂.

A similar experiment was carried out in an atmosphere of CO₂ and the generated gas collected in an azotometer filled with a concentrated solution of potassium hydroxide. We found 81% and 82.5% of the theoretical amount of nitrogen.

Eindhoven, January 1949.

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⁴⁾ J. *Vaughan* and L. *Phillips*, J. Chem. Soc. (1947) II, 1560.