A Note on the Fowler's Solution of the Lane-Emden Equation of Index 3

In this note, the validity of the FOWLER's solution is extended to a larger region around the centre. A series solution is also sought in the (ξ, θ) plane, which covers the FOWLER's solution near the origin[1].

The Lane-Emden differential equation for $n = 3$ is

$$y \frac{dy}{dz} + y + z^3 = 0 , \qquad (1)$$

where

$$y = \frac{dz}{dt} , \quad z = \xi\theta = \theta e^{-t} .$$

Applying the HARDY's[2] theorem that $dy/dz \to 0$ as $t \to \infty$ or $\xi \to 0$ for the algebraic differential equation (1), FOWLER[3] obtained the approximate solution $\theta \sim 1/\xi$ $(2 \log C/\xi)^{-1/2}$ near the origin, where C is a constant of integration. Now we seek a solution valid in a larger region $-1 < dy/dz < 1$ around the origin $\xi = 0$. The equation (1) can be written in the form

$$-\frac{y}{z^3} = 1 - \frac{dy}{dz} + \left(\frac{dy}{dz}\right)^2 - \left(\frac{dy}{dz}\right)^3 + \ldots (-1)^n \left(\frac{dy}{dz}\right)^n + \ldots \qquad (2)$$

We choose a sufficiently large positive integer m such that for $n \geq m$, $(dy/dz)^n \to 0$ in the region $-1 < dy/dz < 1$. If we substitute for dy/dz from (1) in (2) and sum up the terms, we get

$$(y + z^3)^m = 0 \quad \text{or} \quad y = \frac{dz}{dt} = -z^3 , \qquad (3)$$

which, on integration, yields a solution in the (ξ, θ) plane in the form

$$\theta = \frac{1}{\xi} \left[\frac{1}{2 \log C/\xi}\right]^{1/2} , \qquad (4)$$

where C is a constant of integration. The solution (4) includes the FOWLER's solution near the centre and thus extends the validity of the FOWLER's approximation to a larger region around the centre.

The homology theorem shows that we can take $z = 1$ at $t = 0$ without any loss of generality. Therefore, at $t = 0$, we can assume a Taylor's expansion of the form

$$z = 1 + z_0^{(1)} t + \frac{1}{2!} z_0^{(2)} t^2 + \frac{1}{3!} z_0^{(3)} t^3 + \frac{1}{4!} z_0^{(4)} t^4 + \ldots \qquad (5)$$

where $z_0^{(n)}$ stands for the value of nth derivative of z at $t = 0$. Calculating different derivatives with the help of (3) and substituting in (5), we get

$$z = 1 - t + \frac{3}{2} t^2 - \frac{5}{2} t^3 + \frac{35}{8} t^4 - \frac{63}{8} t^5 + \ldots$$

or reverting to the (ξ, θ) plane we obtain

$$\theta = \frac{1}{\xi} \left[1 + \log \xi + \frac{3}{2} (\log \xi)^2 + \frac{5}{2} (\log \xi)^3 + \frac{35}{8} (\log \xi)^4 + \ldots\right] . \qquad (6)$$

The series solution given by (6) is in full agreement with the FOWLER's approximate solution near the origin and with the solution given by (4) towards the centre as well as towards the boundary.

Zusammenfassung. Für FOWLER's Lösung der Lane-Emden-Gleichung von Index 3 wird der Gültigkeitsbereich erweitert.

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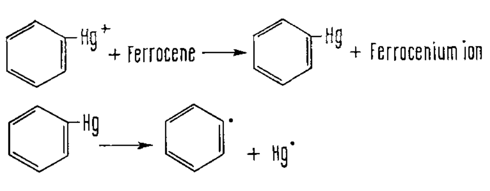
[2] G. H. HARDY, Camb. Tracts Math. *12*, 57 (1924).

[3] R. H. FOWLER, Q. Jl. Math. *2*, 259 (1931).

Reduction of Benzene Tetrakis-Mercuric Acetate with Ferrocene

It is well known that solvolysis of alkylmercuric salts leads to the formation of carbonium ions[1] while arylmercuric salts resist such heterolysis[2]. In the presence of reducing agents such as ferrocene, however, phenylmercuric acetate afforded phenyl radical[3] via the formation of phenylmercury (I) intermediate.



Similar reactions were observed in the solvolysis of triethyllead acetate and subsequent reduction of the triethyllead cation to form triethyllead which further fragments to diethyllead and ethyl radical[4]. In this paper we wish to report that solvolysis and reduction of benzene tetrakismercuric acetate have led to the formation of benzyne type intermediate.

When the synthesis of phenylene-1, 2-dimercuric acetate was attempted by reacting mercuric acetate and benzene under various conditions[5], it always resulted in the formation of a mixture of unidentifiable products. However, when mercuric acetate (Merck, Reagent grade)

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[1] F. R. JENSEN and R. J. OUELLETTE, J. Am. chem. Soc. *83*, 4477, 4478 (1961).

[2] J. H. ROBSON and G. F. WRIGHT, Can. J. Chem. *88*, 21 (1960).

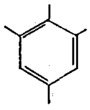
[3] C.-H. WANG, J. Am. chem. Soc. *85*, 2339 (1963).

[4] C.-H. WANG, P. LEVINS and H. G. PARS, Tetrahedron Letters *12*, 687 (1964).

[5] R. CUISA and G. GRILLO, Gazz. chim. ital. *57*, 323 (1926).

was added to molten diphenylmercury, 2 g, mp 121–122° (Chemical Procurement Laboratories), it produced a white solid, 2.8 g. The solid was dissolved in aqueous ammonium acetate solution (50 g of ammonium acetate in 50 ml of water) and reprecipitated by acidifying the solution with acetic acid to pH 5. Analytical sample, melting at 270° with decomposition, was obtained by recrystallization several times as described above. Analysis[6], calculated for $C_{14}H_{14}O_8Hg_4$: C, 15.15; H, 1.26; Hg, 74.4. Found: C, 14.85; H, 1.30; Hg, 73.9. No phenylene-1,2-dimercuric acetate was isolated under any conditions.

Because of the extremely low solubility of the compound, effort utilizing NMR spectroscopy to determine which of the 3 possible isomers (I, II and III) were obtained was unsuccessful, but it is clear that all of them have substituent groups at the *ortho* position to each other.



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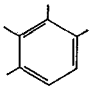

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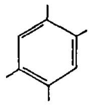
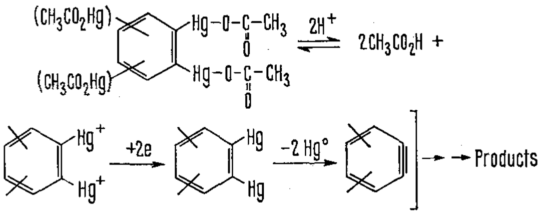
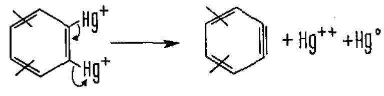


III

Solvolysis and reduction of the compound were carried out in the form of suspension in methanol under nitrogen atmosphere. In a typical run, a slurry of 0.26 g (2.4×10^{-4} moles) of benzene tetrakis-mercuric acetate and 0.19 g (1.02×10^{-3} moles) of ferrocene (Aldrich Chemical Company, mp 172–174°) in 5 ml of methanol containing trace amount of *p*-toluenesulfonic acid (Matheson Coleman and Bell) under nitrogen atmosphere in a pressure bottle was placed in an oven at 60 °C for 48 h. In the accompanying blank run, all the conditions were identical except ferrocene was not present. The gradual appearance of the blue ferrocenium ion color in the reaction flask was observed. At the end of the reaction period, the reaction mixture appeared black while the blank run was only slightly tinted. The reaction mixture was filtered and the solid was washed with methanol. The filtrate and the washing solution were combined. An aliquot of 3 μl of the methanol solution was injected into a F. and M. chromatograph, Model 609, with a 5 ft and $1^1/_2$ in column of 20% carbowax 20 m on chromosorb w 60/80; helium as carrier gas, 35 ψ, flow rate 70 ml/min; temperatures: column 190 °C, injector 274 °C, and detector 348 °C. Two peaks in the chromatogram, not found in the blank run, were identified as anisole (4%) and benzyl alcohol (82%). No benzene was detected. In toluene, the reaction was carried out under comparable conditions and the yield of diphenylmethane was almost quantitative. No benzene was found in the reaction mixture. It is known that phenyl radical abstracts hydrogen atoms from solvents such as toluene or phenylates aromatic rings[7]. The formation of addition compounds by phenyl radical with solvent such as methanol or toluene was never reported. This intermediate, presumably resulting from simultaneous solvolysis and reduction of the *ortho* substituent groups, differs in behavior from the benzyne intermediate generated from different precursor under different conditions. For example, the benzyne intermediate from the decomposition of benzenediazonium salts in alcohols forms phenylalkyl ethers[8]. In the present experiments, the formation of benzyl alcohol in methanol and diphenylmethane in toluene by this intermediate can be envisioned as a result of benzyne insertion to carbon-hydrogen bonds. This observation resembles the formation of arylpiperidines by arynes in piperidine[9] which can be considered as insertion of nitrogen-hydrogen bonds by benzyne intermediate. It is generally believed that extremely reactive chemical species generated by different processes and from different sources may not be electronically the same[10]. The remaining 2 mercuric acetate groups probably follow the same reaction route as in phenylmercuric acetate[3] forming phenyl radicals which eventually abstract hydrogen atoms from the solvent molecules.



It is also possible that the intermediate is formed through an ionic elimination mechanism.



This mechanism seems unlikely since in the blank runs where ferrocene was absent, the mercury compound in methanol and toluene did not yield the corresponding products, benzyl alcohol and diphenylmethane.

In acetic acid, the products identification was less conclusive. The difficulty here might at least be partially due to the unfavorable solvolysis of the parent compound in this solvent and thus the reduction of the cation by ferrocene was prevented. When the reaction was carried out in furan at room temperature under nitrogen atmosphere with vigorous stirring for a period of several days, it gave a rather complex mixture from which well-defined products could not be isolated. It was possible, however, to demonstrate the presence of a very small amount of the anticipated adduct, 1,4-dihydronaphthalene-1,4-endoxide by converting to α-naphthol[11]. α-Naphthol was identified by comparison of its UV spectrum with that of an authentic sample[12].

Résumé. La solvolyse et la réduction éventuelle du tétrakis-acétate de mercure de benzène avec le ferrocène conduisent à la formation d'une part de benzyl-alcohol et d'anisole au sein du méthanol et d'autre part à la production de diphénylméthane au sein du toluène. L'origine de ces produits est discutée.

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Boston (Massachusetts 02116, USA), 15 December 1969.

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[6] Analyses are by S. M. NAGY of Massachusetts Institute of Technology and melting points are uncorrected.

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[13] To whom inquiries should be directed at the University of Massachusetts at Boston.