Tetrahedron Letters No.19, pp. 2095-2100, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ON THE ALLEGED EXISTENCE OF THE RADICAL-ANIONS OF CYCLOPROPANE, ADAMANTANE AND HEXAMETHYLENETETRAMINE

F. Gerson, E. Heilbronner and J. Heinzer

Laboratorium für organische Chemie der Eidg. Technischen
Hochschule, Zürich

(Received 7 March 1966)

Bowers et al. have reported the preparation of the radical anions of cyclopropane [1], of adamantane [2] and of hexamethylenetetramine [2]. In a recent letter Jones [3] has shown that the esr spectrum attributed to the radical anion of adamantane is due to small traces of benzene. This proof relies on the fact that the spectra obtained for the "adamantane radical anion" at various temperatures (-110° to -180°) in the solvent mixture dimethoxyethane/tetrahydrofurane (1:2) are identical with those of benzene radical anion. We would like to corroborate this conclusion and to extend it to the alleged radical anions of cyclopropane and hexamethylenetetramine by reporting that the esr signal obtained for a solvated electron in dimethoxyethane cannot be quenched by arbitrary amounts of cyclopropane, adamantane or hexamethylenetetramine.

It is well established that potassium or potassium-sodium alloys dissolve in certain ethers yielding blue solutions, which exhibit to some degree the properties of alkali metal solutions in liquid ammonia [4]. An example is furnished by dissolving potassium at low temperatures (-60° to -90°C) in 1, 2-dimethoxyethane (DME):

$$(1)\quad K + DME \rightleftharpoons K^{\oplus} + [e^{\ominus}; DME]$$

$$(2)\quad 2[e^{\ominus}; DME] \rightleftharpoons [e_2^{\ominus\ominus}; DME]$$

$[e^{\ominus}; DME]$ stands for an unpaired solvated electron and $[e_2^{\ominus\ominus}; DME]$ for a solvated electron pair. The equilibrium (2) is shifted almost completely towards the right side leaving only a very small concentration of the paramagnetic species[4]. A weak esr signal, 0.4 gauss in width, which is due to $[e^{\ominus}; DME]$ can, however, be observed in such solutions[5]. An increase in the temperature of the sample leads to disappearance of the signal and to fading of the blue colour. On the other hand, addition of tetrahydrofurane to the blue solution quenches the esr signal without diminution in the colour intensity. This supports the suggestion[4] that the blue colour cannot be attributed solely to the small concentration of unpaired electrons, but it is due to the totality of solvated electrons, unpaired and paired.

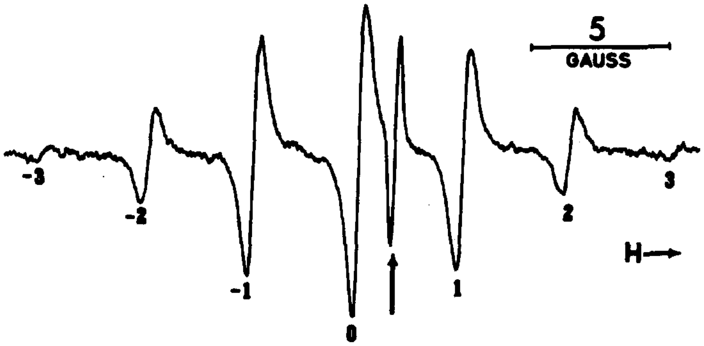
If small amounts of aromatic hydrocarbons (e. g. perylene) are introduced into the blue solution of potassium in dimethoxyethane, the colour changes to that of the corresponding radical anion of the hydrocarbon and the weak esr signal of the unpaired solvated electrons is replaced by a very intense spectrum of the anion.

$$(3)\quad Ar + \left\{\begin{matrix}[e^{\ominus}; DME] \\ \upharpoonleft\downharpoonright \\ [e_2^{\ominus\ominus}; DME]\end{matrix}\right\} \longrightarrow Ar^{\ominus} + DME$$

On addition of a minute amount of an aromatic hydrocarbon of low electron affinity, e.g. benzene, the effectively one sided reaction (3) becomes a true equilibrium:

$$\text{(4)}\quad \text{Benzene} + \left\{ \begin{array}{c} [e^{\ominus};\ \text{DME}] \\ \upharpoonleft\!\downharpoonright \\ [e_2^{\ominus\ominus};\ \text{DME}] \end{array} \right\} \rightleftharpoons \text{Benzene}^{\ominus} + \text{DME}$$

The concentration of $[e^{\ominus};\ \text{DME}]$ and of benzene are such as to give rise simultaneously to observable esr signals for both species. As expected, the equilibrium (4) is temperature-dependent: cooling of the solution favours the formation of the benzene radical anion. An esr spectrum obtained at -85° is shown below.



The hyperfine components of benzene radical anion are numbered. The signal of the solvated electron is indicated by an arrow.

From these results the conclusion can be drawn that the electron affinity of benzene under the conditions of the experiment is comparable to that of the acceptor sites in the solvent dimethoxyethane.

In sharp contrast to the behaviour of aromatic hydrocarbons, addition of cyclopropane, adamantane or hexamethylenetetramine in large amounts has no influence whatsoever on the equilibrium (1) and (2). If a minute amount of benzene is present, the equilibrium (4) is also unaffected by arbitrary amounts of the three saturated compounds mentioned. Therefore, we deduce that none of them has an electron affinity comparable with that of benzene or the acceptor sites in dimethoxyethane. This supports Jones' conclusion concerning the anion forming capabilities of adamantane and extends the argument to cyclopropane and to hexamethylenetetramine.

There remains the question: What are the paramagnetic species observed by Bowers et al.1) 2) ?

It has been our experience that dimethoxyethane dried and stored over potassium-sodium alloy always contains trace amounts of benzene which are not removed by radical anion formation at room temperature or by distillation. They give rise to a spectrum similar to that shown in the figure above.

We have repeated the original experiments under the conditions reported by Bowers et al.1) 2) (solvent mixture dimethoxyethane/ tetrahydrofurane 1:2; sodium-potassium alloy; temperature -110° to -160° C) and have observed exclusively the spectrum of the small benzene impurity present in the solvent [6]. The signal of the unpaired solvated electron is absent here for two reasons: 1) Presence of tetrahydrofurane in the solvent mixture and 2) the low temperature, at which the equilibrium (4) is shifted towards the benzene radical anion. However, the blue colour of the solution persists under these conditions.

In the case of adamantane we agree with Jones [3] that the esr spectrum obtained by Bowers et al. [2] is due to benzene, but we believe that adamantane is not the source of the benzene impurity. In our experiments, there was no increase in the intensity of the esr signals of benzene radical anion on adding large amounts of highly purified adamantane.

As for cyclopropane, the large difference between the coupling constants reported by Bowers et al. [1] (2,3 gauss) and those expected for benzene radical anion under the same conditions (3,9 gauss) seems to exclude the possibility that the latter is the species observed (barring a huge error in calibration). Likewise, we are at a loss to account for the spectrum attributed to hexamethylenetetramine [2].

Support was provided by the Schweizerischen Nationalfonds (Projekt Nr. 3745).

1) K. W. Bowers and F. D. Greene, *J. Amer. Chem. Soc.* **85**, 2331 (1963).

2) K. W. Bowers, G. J. Nolfi and F. D. Greene, *J. Amer. Chem. Soc.* **85**, 3707 (1963).

3) M. T. Jones, *J. Amer. Chem. Soc.* **88**, 174 (1966).

4) J. L. Down, J. Lewis, B. Moore and G. Wilkinson, *Proc. Chem. Soc.* **1957**, 209; *J. Chem. Soc.* **1959**, 3767; F. A. Cafasso and B. R. Sundheim, *J. Chem. Phys.* **31**, 809 (1959); S. F. Dainton, D. M. Wiles and A. N. Wright, *J. Chem. Soc.* **1960**, 4283.

5) T. R. Tuttle jr. and S. I. Weissman, *J. Amer. Chem. Soc.* **80**, 5342 (1958). The signal found by these authors was 2 gauss wide.

6) We were able to confirm the observations reported by Jones 3) concerning the freezing point of the sample as well as the temperature dependence of the line shapes and splitting constants in the esr spectrum of benzene radical anion.