

Electron Spin Resonance of the Radical Ion Formed by the Reaction of Hexamethylbenzene with Sulfuric Acid

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Electron spin resonance (e.s.r.) spectra have been obtained for the stable free radical formed by the reaction of hexamethylbenzene (HMB) with 98% H_2SO_4 . The proton coupling constants for this radical were determined to be: 12H, $a_1 = 3.36$ gauss; 6H, $a_2 = 1.68$ gauss; and 2H, $a_3 = 5.40$ gauss. The e.s.r. of HMB in D_2SO_4 showed that only 2 of the 20 protons in the radical exchange with deuterium. The same HMB radical has also been shown to form from HMB in $SbCl_5-CD_2Cl_2$ and from HMB in molten I_2 . The formation of the HMB radical under aprotic conditions shows that all 20 protons in the radical originate from HMB molecules through molecular rearrangements. N.m.r. measurements have also confirmed the occurrence of methyl rearrangement reactions for HMB in acidic media. The radical formed from HMB in H_2SO_4 is proposed to be the hexamethylbenzyl (4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5) radical cation. The structure of this radical is consistent with the e.s.r. assignment and with the selective line broadening phenomena observed in the e.s.r. spectrum. It is concluded that free-radical intermediates may play an important role in acid-catalyzed rearrangement reactions of methylbenzenes.

I. Introduction

We have found that hexamethylbenzene (HMB) reacts with concentrated H_2SO_4 to form a deeply colored solution which exhibits an intense electron spin resonance signal. This signal was not that of the simple HMB cation. This paper describes the results of e.s.r. studies for HMB in H_2SO_4 and discusses the structure of the stable radical cation formed from HMB in oxidizing media.

Electron spin resonance spectra have been reported for the stable unipositive radical ions of a number of polycyclic hydrocarbons in H_2SO_4 solution.^{1,2} Although the anions of benzene and its methylated derivatives have been studied by e.s.r.,³⁻⁵ the oxidation of monocyclic aromatics to radical cations has been difficult to achieve. Benzene derivatives are not oxidized by 98% H_2SO_4 . Methylated benzenes can be oxidized with stronger reagents, such as $K_2S_2O_8-H_2SO_4$, but these reactions produce semiquinones.^{6,7}

Recently, Hulme and Symons⁸ reported the e.s.r. of

(1) S. I. Weissman, E. de Boer, and J. J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957).

(2) A. Carrington, F. Dravineks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(3) T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

(4) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

(5) J. R. Bolton, *J. Chem. Phys.*, **41**, 2455 (1964).

(6) J. R. Bolton and A. Carrington, *Proc. Chem. Soc.*, 174 (1961).

(7) J. A. Brivati, R. Hulme, and M. C. R. Symons, *ibid.*, 384 (1961).

(8) R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1120 (1965).

the HMB cation prepared by the photolysis of HMB in 98% H_2SO_4 . Carter and Vincow⁹ also observed the e.s.r. of the HMB cation prepared in fuming H_2SO_4 .

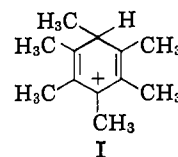
We have found that although HMB does not react immediately with 98% H_2SO_4 , it does undergo a slow rearrangement to form a stable radical which is not the simple HMB cation. This reaction is related to the rearrangements found for other methylbenzenes in strong oxidizing environments.^{10,11}

To supplement our e.s.r. studies of the HMB- H_2SO_4 system, we have also carried out optical absorption and n.m.r. experiments. In section II, the optical spectra of HMB in 98% H_2SO_4 are described. In section III, the e.s.r. results for HMB in H_2SO_4 are described. In section III, the e.s.r. results for HMB in H_2SO_4 and HMB in D_2SO_4 are discussed. Section III also presents e.s.r. data for HMB in two other oxidizing media, $SbCl_5$ and I_2 . In section IV, n.m.r. results for the ions formed from HMB with strong acids are described. Finally, in section V, a structure of the radical from HMB is proposed and the evidence in support of this structure is given.

II. Optical Spectra of Hexamethylbenzene in H_2SO_4

The optical spectra of HMB in H_2SO_4 show that HMB initially protonates in 98% H_2SO_4 and that the protonated HMB ion then undergoes further reaction to form a second species which is a free radical.

The ultraviolet-visible absorption spectra obtained for HMB in concentrated H_2SO_4 over a period of 24 hr. are shown in Figure 1. Hexamethylbenzene dissolves initially in H_2SO_4 to form a yellow solution. The spectrum of this solution (0 hr.) contains absorption bands at 393 and 280 $m\mu$. These bands can be attributed to the protonated HMB cation I. The same



spectrum has been reported for solutions of HMB in CCl_3COOH and in $CF_3COOH-H_2SO_4$ mixtures.¹² After about 1 hr., the solution of HMB in H_2SO_4 turns red and develops new absorption bands at 520 and 334 $m\mu$. These new bands increase with time and indicate the formation of a second species, presumably a free radical, in the H_2SO_4 solution. The spectrum obtained for HMB in H_2SO_4 after 3 hr. is also shown in

(9) M. K. Carter and G. Vincow, *Bull. Am. Phys. Soc.*, [2] **10**, 374 (1965).

(10) O. Jacobsen, *Chem. Ber.*, **19**, 1209 (1886).

(11) L. I. Smith, *Org. Reactions*, **1**, 370 (1942).

(12) M. Kilpatrick and H. H. Hyman, *J. Am. Chem. Soc.*, **80**, 77 (1958).

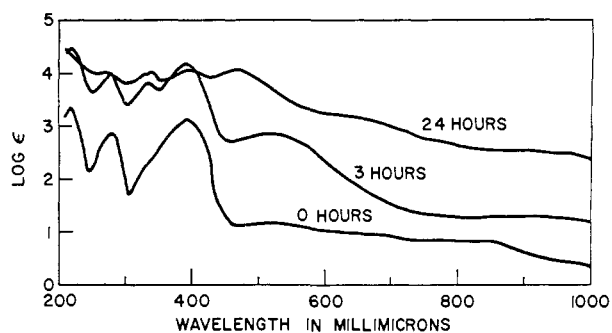


Figure 1. Optical spectra of HMB in H_2SO_4 .

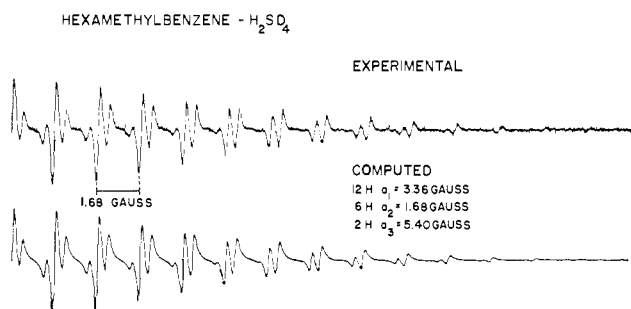


Figure 2. E.s.r. of HMB in H_2SO_4 ; comparison between experimental curve and curve synthesized by an s.e.s.r.s. computation.

Figure 1. After 24 hr., the spectrum becomes quite complex as a result of further oxidation reactions.

III. Electron Spin Resonance Results

Hexamethylbenzene in H_2SO_4 . No e.s.r. signal was observed in the yellow solution of HMB in H_2SO_4 . The red solution exhibited an intense e.s.r. signal, which was stable for several days. The upper curve in Figure 2 shows one-half of the e.s.r. spectrum. This complex pattern was not expected since the six equivalent methyl groups of a HMB radical cation should give rise to 19 equally spaced lines having a binomial intensity distribution.¹³ Figure 3 shows a line representation of the experimental spectrum. There are three groups of lines separated by 5.40 gauss with heights in the ratio 1:2.8:1. The individual lines within each group are spaced 1.68 gauss apart. The three groups of lines in Figure 3 result from a 5.40-gauss splitting by two equivalent protons.

To complete the analysis of this spectrum, it is necessary to consider only the central group, since the relative intensities of corresponding lines in each group are identical. The intensities of lines within the central group fall off extremely gradually. This result is illustrated in Figure 4, which compares the experimental intensity distribution with three possible assignments of coupling constants. The lines and bars in Figure 4 represent the experimental intensities. The lower two dashed curves show the intensity distributions for 18 and 36 equivalent protons with coupling constants of 1.68 gauss. It is apparent that the decrease in intensities for both assignments is much more rapid than for the experimental lines.

(13) R. Hulme and M. C. R. Symons⁸ also observed a second stable radical species in their studies of the HMB cation.

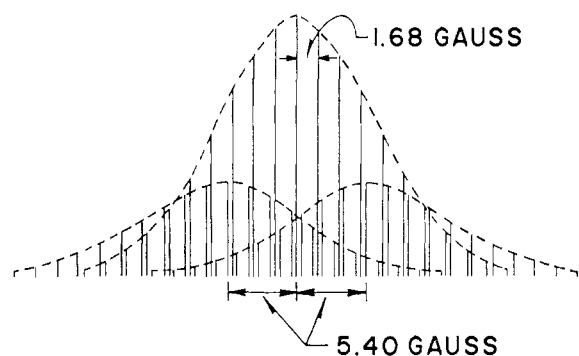


Figure 3. Experimental line spectrum of HMB in H_2SO_4 ; line positions and amplitudes taken from the upper spectrum in Figure 2.

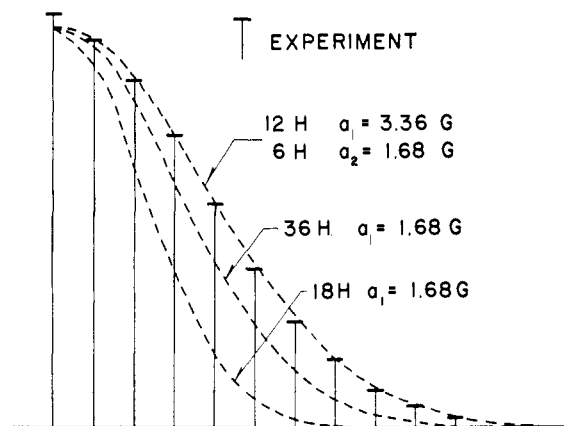


Figure 4. Line intensities of the central group of lines in Figure 3; comparisons with those computed from three different sets of coupling constants (dashed curves).

The upper dashed curve is the intensity distribution for a radical containing 12 protons with $a_1 = 3.36$ gauss and 6 protons with $a_2 = a_1/2 = 1.68$ gauss. It can be seen that this assignment is in excellent agreement with experiment. Although this 12-6 assignment predicts 31 lines, our experimental signal-to-noise ratio permitted the observation of only 21 lines.

Considerable effort was required to show that the 12-6 assignment was unique. Figure 5 shows correlation diagrams for the lines within the central group for various chemically reasonable assignments. These diagrams show the per cent deviation between intensities of corresponding lines of the experimental and computed spectra. It can be seen that the correlation diagram for the 12-6 assignment is the only one in which the deviations are small and random.

As previously mentioned, the relative amplitudes of the three major groups of lines in Figure 3 are appreciably different from the 1:2:1 ratio to be expected from a splitting by two equivalent protons. It was noted, however, that the e.s.r. lines belonging to the outer groups were slightly wider than those in the central group. A 10-20% greater width of the outer lines would account for the observed deviation from an exact 1:2:1 ratio of amplitudes. These observed line-width variations suggest that there may be restricted rotation involving the two protons which give rise to the large splitting.¹⁴ One might expect such

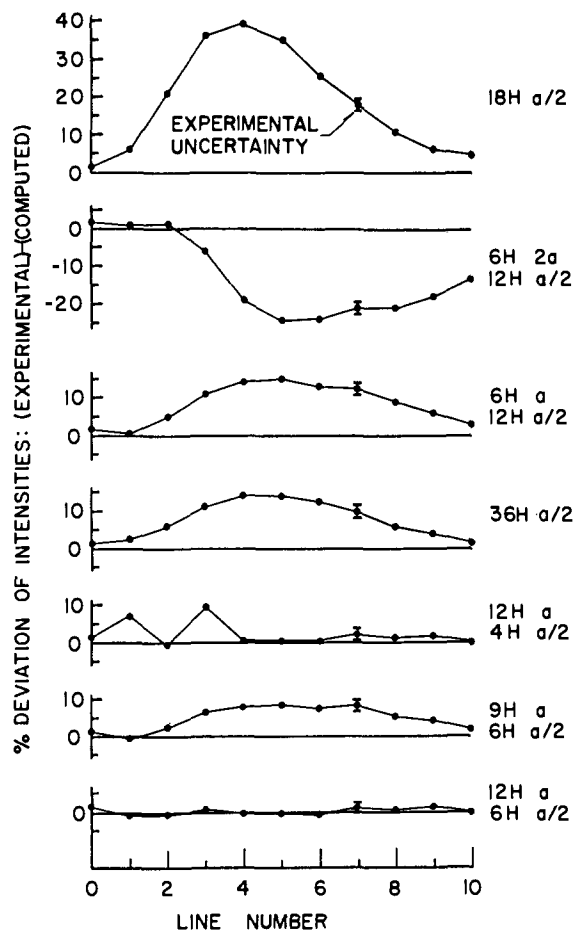


Figure 5. Correlation diagrams for the intensities of the central group of lines in the e.s.r. spectrum of HMB in H_2SO_4 ; line number zero is the central line of the spectrum. The spacing $a/2$ equals 1.68 gauss.

line-width variations to depend upon both temperature and viscosity. Figure 6 shows the central portion of the HMB spectrum at three different temperatures. Note that the width of the intense lines, which belong to the central group, do not vary with temperature. The satellite lines which belong to the outer groups narrow considerably with increasing temperature. At 54° , the ratios of the amplitudes for the three main groups of lines are within 15% of the expected 1:2:1 distribution. It was also found that the addition of trifluoroacetic acid to a solution of the radical in H_2SO_4 lowered the room temperature viscosity sufficiently to decrease the widths of the satellite lines.

From the earlier discussion, it was concluded that the e.s.r. spectrum of the radical formed from HMB in H_2SO_4 had the following coupling constants: 12H , $a_1 = 3.36$; 6H , $a_2 = 1.68$; and 2H , $a_3 = 5.40$ gauss. Final confirmation of this assignment is shown in Figure 2 in which a spectrum simulated from these coupling constants is compared with the experimental curve obtained at 25° . The synthesized s.e.s.r.s. (simulation of electron spin resonance spectra) curve¹⁵ contains two different line widths: 0.157 gauss for the central group and 0.174 gauss for the two outer groups.

(14) J. H. Freed and G. K. Fraenkel, *J. Am. Chem. Soc.*, **86**, 3477 (1964).

(15) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

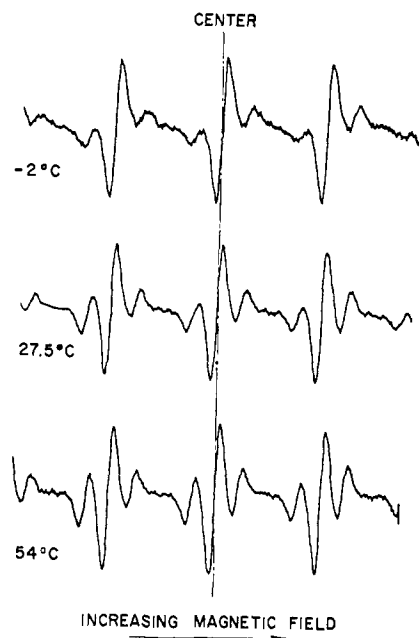


Figure 6. Central portion of the e.s.r. spectrum of HMB in H_2SO_4 at three different temperatures.

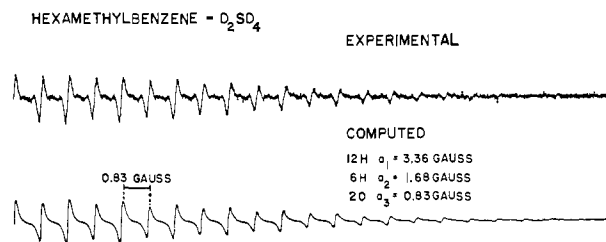


Figure 7. E.s.r. of HMB in D_2SO_4 ; comparison between experimental curve and curve synthesized by an s.e.s.r.s. computation.

Hexamethylbenzene in D_2SO_4 . The 12-6-2 assignment of coupling constants shows that the observed radical contains two more protons than the original hexamethylbenzene molecule. In order to determine whether the additional two protons involved the H_2SO_4 solvent, an e.s.r. spectrum was obtained for HMB in D_2SO_4 . The upper curve in Figure 7 shows one-half of the experimental spectrum. There is no sign of the three groups of lines shown in Figure 3; instead, 37 equally spaced lines with a separation of about 0.84 gauss are observed.

The spectrum of HMB in D_2SO_4 is consistent with the previous 12-6-2 assignment only if the two protons which give rise to the large 5.4-gauss splitting are replaced by deuterons. Since the ratio of the deuterium coupling constant a_D to the proton coupling constant a_H is given by

$$\frac{a_D}{a_H} = \frac{\mu_D I_H}{\mu_H I_D} = \frac{0.8574(1/2)}{2.7927(1)} = 0.1535$$

the $a_H = 5.4$ -gauss splitting becomes $a_D = 0.83$ gauss. This predicted splitting agrees within experimental error with the measured 0.84-gauss spacing. The particularly simple spectrum in Figure 7 results from the fact that the 0.84-gauss deuteron splitting is precisely one-half of the smallest proton splitting of 1.68 gauss.

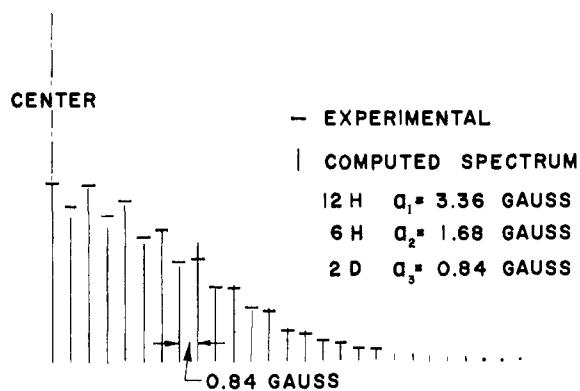


Figure 8. Line intensities for the e.s.r. of HMB in D_2SO_4 ; comparison between experimental (taken from the upper curve in Figure 7) and computed spectra.

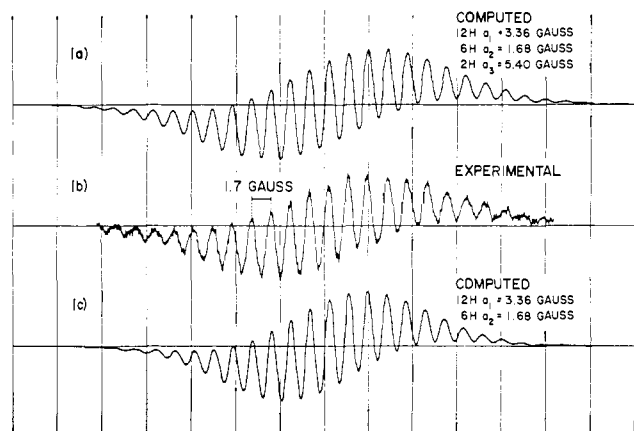


Figure 9. E.s.r. of a $3 \times 10^{-3} M$ solution of HMB in molten I_2 at 125° ; comparison between experimental curve and two curves synthesized by s.e.s.r.s. computations.

In Figure 8, the experimental line intensities taken from Figure 7 are compared with a line spectrum computed from a 12H, 6H, 2D assignment. The alternation in line intensity is a result of the 1:2:3:2:1 distribution of intensities for two equivalent deuterons of spin 1. Final confirmation of the assignment is given in Figure 7, which shows an s.e.s.r.s. comparison of the computed and experimental spectra.

The most likely explanation of the D_2SO_4 results is that the two additional protons (deuterons) in the HMB radical arise directly from the H_2SO_4 (D_2SO_4) solvent. However, in view of the known ease of rearrangement of methylbenzenes in H_2SO_4 ,¹¹ another possibility is that these two protons result from intermolecular methyl addition reactions. This second alternative would then require that of the 20 protons in the HMB radical, only the two with the 5.4-gauss splitting readily exchange with D_2SO_4 . To distinguish between these alternatives, we prepared the HMB radical species in two media which do not contain exchangeable protons.

Hexamethylbenzene with Iodine and with $SbCl_5$. Two aprotic reagents which have been employed as electron acceptors for the preparation of aromatic radical cations are I_2 ¹⁶ and $SbCl_5$.¹⁷ Figure 9b shows

(16) J. Kommandeur, *Mol. Phys.*, **4**, 509 (1961).

(17) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, in press.

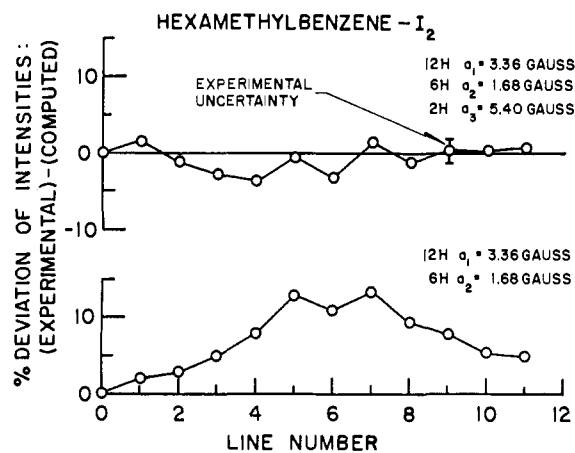


Figure 10. Correlation diagrams for the e.s.r. spectrum of HMB in molten I_2 . Intensities taken from the curves in Figure 9. Line number zero is the central line of the spectrum.

the e.s.r. spectrum which we have obtained for a $3 \times 10^{-3} M$ solution of HMB in molten I_2 at 125° . The spectrum consists of at least 23 equally spaced lines about 1 gauss wide with a separation of 1.7 gauss. The spectrum is incompletely resolved, but the 1.7-gauss spacing is, within experimental error, identical with the 1.68-gauss splitting observed for HMB in H_2SO_4 .

Because of the poor resolution the individual satellite lines arising from the 5.40-gauss splitting cannot be discerned. To ascertain whether this two-proton splitting is present in the HMB- I_2 spectrum, an s.e.s.r.s. comparison, which takes into account the incomplete resolution, was performed. This comparison is shown in Figure 9. It can be seen that the line intensities for the spectrum c in which the two-proton splitting is omitted fall off more rapidly than in the experimental curve b. On the other hand, the s.e.s.r.s. spectrum a for the 12-6-2 assignment is in agreement with experiment. Figure 10 shows a quantitative comparison (correlation diagram) of the experimental and computed line intensities taken from Figure 9. This comparison confirms the 12-6-2 assignment for the HMB- I_2 spectrum.

When a dilute solution of HMB in CD_2Cl_2 is treated with $SbCl_5$, a red color develops and the sample exhibits an e.s.r. signal identical with that for HMB in H_2SO_4 (Figure 2). The e.s.r. observations with I_2 and $SbCl_5$ prove that all 20 protons in the HMB radical arise from HMB molecules. Since only two of the protons exchange with deuterium in D_2SO_4 , their bonding must be quite different from that of the other 18 protons.

g-Factors. The *g*-factor of the radical formed from HMB in H_2SO_4 (Figure 2) was determined to be 2.0024 ± 0.0001 . Within experimental error, this value is identical with that found for hydrocarbon positive ions.¹⁸ This *g*-factor eliminates the possibility that the HMB radical is a quinone cation similar to that formed by the oxidation of *p*-xylene in H_2SO_4 - $K_2S_2O_8$ solution.^{6,7} Oxygen-containing free radicals generally have considerably higher *g*-values, viz., between 2.0034 and

(18) M. S. Blois, H. W. Brown, and J. E. Maling, "Free Radicals in Biological Systems," Academic Press Inc., New York, N. Y., 1961, p. 117.

2.0047.¹⁸ The *g*-factor of the duroquinone cation has recently been found to be 2.00336 ± 0.0001 .⁸ These *g*-factor results show that the radical from HMB does not contain oxygen.

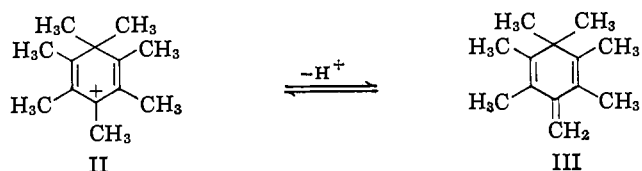
The *g*-factor for the HMB radical in molten I₂ had the unusually high value of 2.0057. However, we have found anomalously high *g*-factors for other radical cations in molten iodine. For example, the perylene radical cation in molten I₂ had the remarkably high *g*-value of 2.0090 ± 0.0003 . The large spin-orbit coupling constant of iodine¹⁸ may be responsible for the large positive *g*-shifts when molten I₂ is used as a solvent.

IV. N.m.r. Studies of the Reactions of Hexamethylbenzene with Strong Acids

The e.s.r. coupling constant assignment for the radical ion from HMB shows that HMB must undergo molecular rearrangement in strongly acidic media. To obtain additional evidence for rearrangement reactions of HMB in oxidizing media, we have measured the n.m.r. of HMB in H₂SO₄ and in SbCl₅-CH₂Cl₂.

Rearrangement reactions of methylbenzenes in strong acids (Jacobsen reaction) are well known.^{10,11} Furthermore, the mechanism of these rearrangements has been postulated to involve free-radical intermediates.¹⁹ Several recent n.m.r. studies have demonstrated chemical exchange and rearrangement reactions of HMB in the presence of strong acids. Maclean and Mackor²⁰ studied the n.m.r. of HMB in HF-BF₃ at -85° and obtained a resolved spectrum of the protonated hexamethylbenzenium ion (I).

At room temperature, the n.m.r. spectrum collapsed to a single peak due to rapid proton-exchange reactions. These exchanges were postulated to occur intramolecularly within the ion I. Birchall and Gillespie²¹ have observed similar effects for solutions of HMB in HSO₃F. However, they postulated a mechanism of exchange in which the proton of I exchanged with the solvent. Doering, *et al.*,²² have reported n.m.r. data for the very stable heptamethylbenzenium ion (II) which result from the rearrangements of methylbenzenes in the presence of Friedel-Crafts catalysts. This ion (II) can alternately be produced from HMB and CH₃OH in H₂SO₄ and can readily be converted to its conjugate base III.



Our n.m.r. studies of HMB in H₂SO₄, D₂SO₄, and SbCl₅-CH₂Cl₂ also show that rearrangement and exchange reactions of HMB occur. In 98% H₂SO₄ at 25°, only a single broad absorption at 2.35 p.p.m. was observed. This peak can be attributed to ion I which is undergoing rapid proton exchange. In

(19) F. Bohlmann and J. Riemann, *Chem. Ber.*, **97**, 1515 (1964).

(20) C. Maclean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

(21) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

(22) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

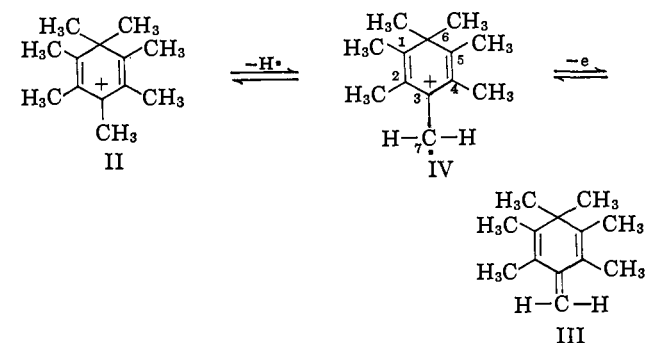
98% D₂SO₄, no methyl resonance was detected, although an H₂SO₄ peak can be observed to grow as the HMB goes into solution. The development of the H₂SO₄ peak demonstrates the presence of solvent-HMB exchange reactions which involved either the radical or the protonated ion I.

Hexamethylbenzene reacts vigorously with a concentrated solution of SbCl₅ in CH₂Cl₂ at room temperature to form a dark, paramagnetic precipitate and a deeply colored solution. The n.m.r. spectrum of this mixture was poorly resolved. However, when the precipitate was filtered, the solution gave a high resolution spectrum which contained five proton peaks at 1.90, 2.61, 2.75, 2.91, and 3.11 p.p.m. and an aromatic proton peak at 7.25 p.p.m. The chemical shifts for the five proton peaks at 1.9 to 3.1 p.p.m. are very similar to those reported for the methyl groups in the HMB cations I^{20,21} and II.²² The resonance at 1.9 p.p.m. is due to an aliphatic out-of-plane methyl group. The remaining peaks are due to aromatic methyl groups. The large downfield chemical shifts observed for these groups show that the HMB species in SbCl₅-CH₂Cl₂ are positive ions.²⁰

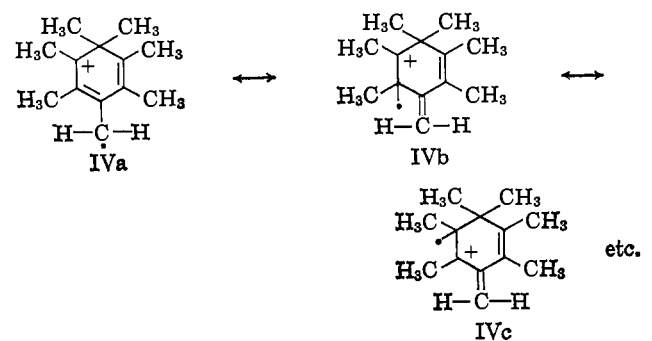
The presence of an aromatic proton peak and the chemical shifts for the methyl protons show the occurrence of demethylation and methyl rearrangement reactions. The large aliphatic methyl peak at 1.9 p.p.m., which is the most intense in the spectrum, definitely confirms the existence of ions of the heptamethylbenzenium type II.

V. Discussion

Our experimental results have led us to conclude that the free radical formed from HMB in H₂SO₄ has structure IV. This radical could readily result from the loss of a hydrogen atom from the heptamethylbenzenium ion II or from a one-electron oxidation of the conjugate base III.



The extreme stability of IV in solution would be expected in view of the reported high stability of the



related positive ion II and the neutral molecule III. The large number of resonance structures which can be written for IV is also consistent with the stability of this radical.

The evidence in favor of the structure IV for the radical ion can be summarized as follows.

1. *The E.s.r. Assignment.* The large splitting of 5.40 gauss can be assigned to the two methylene hydrogens, since a large spin density would be expected at carbon atom number 7. The small splitting of 1.68 gauss can be attributed to the six equivalent protons in the aliphatic methyl groups. The magnitude of this splitting is consistent with that observed for methyl substituents in related aliphatic free radicals.²³ The 12-proton splitting of 3.36 gauss would then be assigned to the four vinyl methyl groups. It is not obvious that all four vinyl methyl groups should give rise to the same proton splitting. From H.m.o. calculations of the related vinylcyclopentadienyl radical, much higher spin densities would be expected at the 1-position than at the 2-position in radical IV. H.m.o. spin densities for the two isomeric unsymmetrical heptamethylbenzyl cations are in even poorer agreement with experiment. The most convincing evidence for the equivalence of the four vinyl methyl groups in IV comes from Doering's observation of identical n.m.r. chemical shifts for the protons in the vinyl methyl groups in the closely related hydrocarbon III.²² The disagreement with H.m.o. theory may be due to the nonplanar conformation of structures III and IV.^{23a}

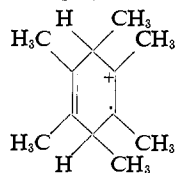
2. *Formation of the Radical in I₂ and SbCl₅.* The observation of the same e.s.r. spectrum for HMB in H₂SO₄, I₂, and SbCl₅-CD₂Cl₂ shows that all 20 protons in the radical must originate from HMB molecules. Since HMB contains only 18 protons, molecular rearrangement must occur. Our n.m.r. studies of HMB with SbCl₅ provide evidence of a rearrangement reaction analogous to that observed by Doering, *et al.*²²

3. *Exchange with D₂SO₄.* The selective exchange of two protons with D₂SO₄ is consistent with structure IV. The methylene carbon, C-7, has considerable double bond character, and the two attached protons should be readily exchangeable with deuterium.

4. *Temperature Dependence of the E.s.r.* The observed line broadening effects are consistent with a radical having the structure IV in which there is hindered rotation of a CH₂ group about a bond with considerable double bond character. The line-width variations shown in Figure 6 indicate that the line widths

(23) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(23a) NOTE ADDED IN PROOF. Another structure which was considered for the radical HMB was the ion



Although this structure meets the symmetry requirements for our spectral assignment, it is not a conjugated system and would not be expected to exhibit the degree of stability of the structure IV.

for the $M = \pm 1$ transitions, associated with the two equivalent protons ($a_H = 5.40$ gauss), were larger than those for the $M = 0$ transitions. The widths of the $M = \pm 1$ lines were also strongly dependent on temperature and viscosity. These selective broadening phenomena arise from the dependence of the proton splittings on the relative orientation of the CH₂ group and the plane of the ring. Since the motions of these two equivalent protons are in-phase correlated, the broadening should be proportional to M^2 ,²⁴ in agreement with our experimental observations. Freed and Fraenkel²⁴ also point out that these line-broadening effects should be observable only when the proton splittings are large and the rotations are slow. Both of these conditions would be fulfilled by the hindered CH₂ group in structure IV.

There was also a very slight asymmetry between the +1 and -1 transitions. This effect was most noticeable for the spectrum at -2° (Figure 6) in which the low-field satellite of the central line is slightly less intense and thus wider than high-field satellite. If it can be assumed that the component of the g-tensor perpendicular to the aromatic ring is less than the average of the in-plane components,²⁵⁻²⁷ we are led to the result that the CH₂ proton coupling constants are negative. This result is in agreement with theory²⁸ and with experimental results on irradiated malonic acid^{29,30} and diphenylpicrylhydrazyl.^{31,32}

VI. Conclusions

The stable radical from the oxidation of HMB is presumed to be the hexamethylbenzyl (4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5) radical ion (IV) which is formed by the rearrangement of HMB in strong Lewis acids. The stability of IV is consistent with similar observations by Doering, *et al.*,²² for the related diamagnetic ion II and its conjugate base III. The observation of this stable radical in the acid-catalyzed rearrangement of HMB suggests that free-radical intermediates may be involved in Jacobsen rearrangements of other methylated benzenes.³³ This proposal has recently been made by Bohlmann and Riemann.¹⁹

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(33) We have observed an e.s.r. spectrum for durene in SbCl₅-CH₂Cl₂ and in H₂SO₄, which is different from the spectrum for IV. This spectrum transforms rapidly into that for the HMB radical IV as a result of methyl rearrangements. Pentamethylbenzene and pentamethylbenzyl chloride were also found to undergo immediate rearrangement in H₂SO₄ to the radical IV.