

INTRAMOLECULAR PROTON EXCHANGE IN AROMATIC CARBONIUM IONS: ISOTOPE EFFECT IN HEXAMETHYLBENZENE

E. L. MACKOR and C. MACLEAN

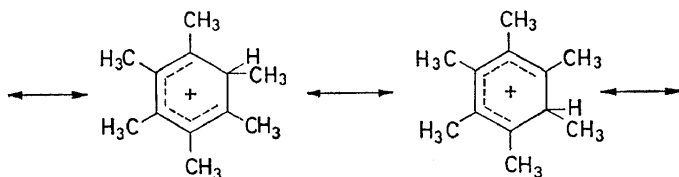
*Koninklijke/Shell-Laboratorium, Amsterdam,
(Shell Internationale Research Maatschappij, N.V.), Holland*

INTRODUCTION

Anhydrous hydrogen fluoride is an attractive solvent for weak bases¹; hexamethylbenzene (HMB), for instance, dissolves in the presence of Lewis acids like BF₃ or PF₅ as its proton complex



in sufficiently high concentrations to study its nuclear magnetic resonance (n.m.r.) spectrum (*Figure 1(a)*)². It was established previously, that the acid proton can be transferred intramolecularly in the proton complex³,



which reaction modifies the n.m.r. spectrum of this ion.

The low-temperature spectrum (*Figure 1(a)*) shows, going from low to high field, the hydrogens of the CH group—a broadened quadruplet caused

by spin-spin couplings with the methyl hydrogens of the $\text{C} \begin{array}{l} \text{H} \\ \diagdown \\ \text{CH}_3 \end{array}$ group (6.8 c/s) as well as with those of the *p*-methyl group (2.0 c/s)—a doublet of the *p*-methyl hydrogens, the signals of *o*- and *m*-methyl hydrogens respectively,

and finally a doublet of the methyl hydrogens of the $\text{C} \begin{array}{l} \text{H} \\ \diagdown \\ \text{CH}_3 \end{array}$ group.

At higher temperatures the spectrum of *Figure 2(a)* is obtained and at intermediate temperatures one measures spectra resembling those of *Figure 3*. It seemed worthwhile to measure the spectra in deuterium fluoride

(Figures 1(b) and 2(b)) in order to study the isotope effect of this relatively simple reaction.

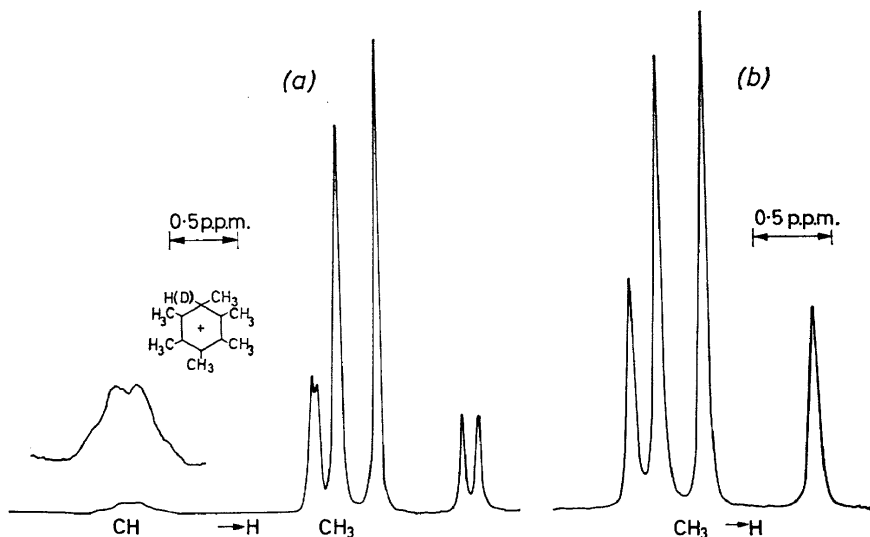


Figure 1. The n.m.r. spectrum of the proton complex of hexamethylbenzene in (a) $\text{HF} \cdot \text{BF}_3$ or (b) $\text{DF} \cdot \text{BF}_3$ at low temperature; field increasing from left to right; scale as indicated

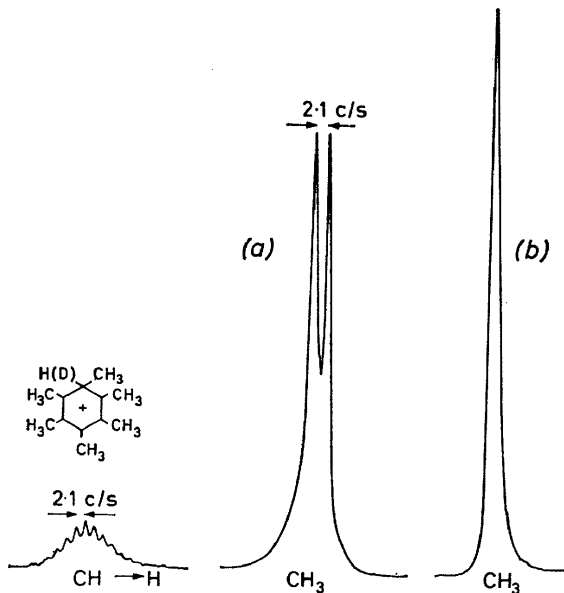


Figure 2. The n.m.r. spectrum of the proton complex of hexamethylbenzene in (a) $\text{HF} \cdot \text{BF}_3$ or (b) $\text{DF} \cdot \text{BF}_3$ at high temperature; field increasing from left to right; scale as indicated

EXPERIMENTAL

Deuterium fluoride was prepared from D_2O and benzoylfluoride⁴;

ISOTOPE EFFECT IN HEXAMETHYLBENZENE

the reactants, mixed at room temperature in a silver vessel, were refluxed for several hours at 120°. Subsequent distillations in Kel-F containers gave DF (2 per cent HF) with trace amounts of D₂O.

Hexamethylbenzene had an estimated purity >99.9 per cent: gas-liquid

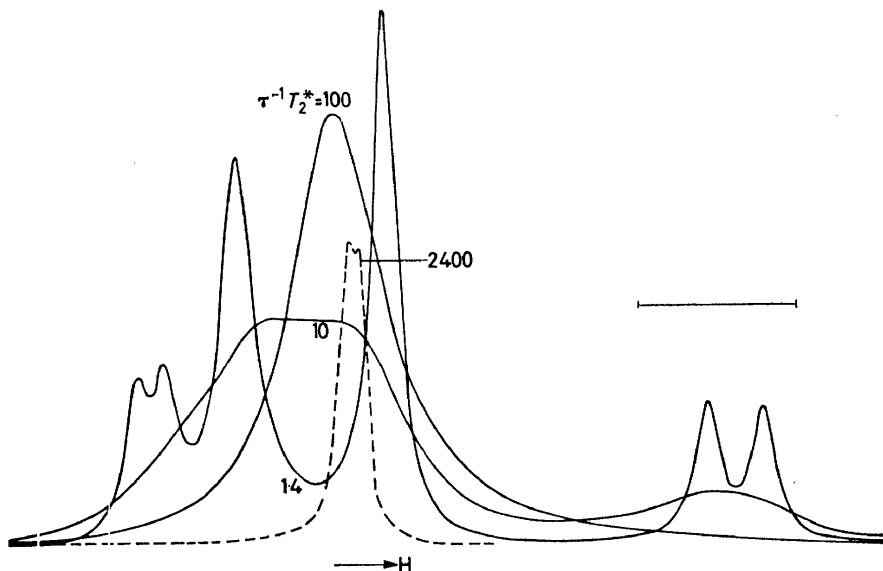


Figure 3. Calculated n.m.r. spectra of the methyl groups of the proton complex of hexamethylbenzene for four values of its lifetime: $\tau^{-1}T_2^* = 1.4; 10; 100; 2400$; the curves correspond with experimental spectra at $-110^\circ, -91^\circ, -75^\circ$ and higher than -55° , respectively; the vertical scale of the dotted peak is one fifth of that of the others; field increasing from left to right; scale (20 c/s) is indicated in the spectra

chromatography gave a single peak. Weighed amounts of hexamethylbenzene were dissolved in HF or DF by adding BF₃ or PF₅; the solutions were prepared in Kel-F capillaries in the absence of oxygen. The solution of HMB in DF/BF₃ with the best isotopic purity contained 2.5 per cent HF.

The solutions, which were kept at dry-ice temperature, were fairly stable; there was no indication of H-D exchange of the methyl groups of HMB in DF. The solutions in HF/BF₃ were pale yellow, as expected from their near-ultraviolet absorption spectrum. There is a slow change over a period of weeks to a darker yellow shade. The solutions in DF/BF₃ were reddish brown, darkening to brown over a period of days. Apparently the DF prepared in the above manner contains traces of oxidizing material. These can be largely removed by letting the impurities in DF react with anthracene (deuterated) and with hexamethylbenzene before distilling the DF into the sample tube containing hexamethylbenzene. The colour of solutions thus prepared is pale yellow, as in HF/BF₃.

The n.m.r. spectra were measured at 56.4 or 60 Mc/s using a Varian HR 60 spectrometer equipped with a variable-temperature Dewar insert.

KINETIC ANALYSIS

The spectrum of the methyl groups consists of two sets of lines, correspond-

ing with the two different spin states (+ or -) of the added proton. The chemical shifts at 60 Mc/s, with respect to the weighted average ($\bar{\nu}^{\pm}$) of the lines, are for the + and - states respectively

$$\begin{array}{ll} \nu_1^+ - \bar{\nu}^+ = -26.9 \text{ c/s} & \nu_1^- - \bar{\nu}^- = -24.7 \text{ c/s} \\ \nu_2 - \bar{\nu}^+ = -13.1 & \nu_2 - \bar{\nu}^- = -14.5 \\ \nu_3 - \bar{\nu}^+ = + 3.9 & \nu_3 - \bar{\nu}^- = + 2.5 \\ \nu_4^+ - \bar{\nu}^+ = +43.5 & \nu_4^- - \bar{\nu}^- = +48.9 \end{array}$$

The kinetic analysis, described in brief in a previous paper³, will now be given in more detail. When the proton is assumed to jump only between adjacent carbon atoms, the Bloch equations, including exchange⁵ are, in standard notation,

$$\frac{d}{dt} G_1^+ + \alpha_1^+ G_1^+ = -\frac{i}{6} \gamma H_1 M_0 + \tau_{31}^{-1} G_3 - \tau_{13}^{-1} G_1^+ \quad (2a)$$

$$\begin{aligned} \frac{d}{dt} G_2 + \alpha_2 G_2 = & -\frac{i}{3} \gamma H_1 M_0 + \tau_{32}^{-1} G_3 + \tau_{42}^{-1} G_4^+ - \\ & - \tau_{23}^{-1} G_2 - \tau_{24}^{-1} G_2 \end{aligned} \quad (2b)$$

$$\begin{aligned} \frac{d}{dt} G_3 + \alpha_3 G_3 = & -\frac{i}{3} \gamma H_1 M_0 + \tau_{13}^{-1} G_1^+ + \tau_{23}^{-1} G_2 - \\ & - \tau_{31}^{-1} G_3 - \tau_{32}^{-1} G_3 \end{aligned} \quad (2c)$$

$$\frac{d}{dt} G_4^+ + \alpha_4^+ G_4^+ = -\frac{i}{6} \gamma H_1 M_0 + \tau_{24}^{-1} G_2 - \tau_{42}^{-1} G_4^+ \quad (2d)$$

$$\alpha_j = 1/T_2^*(j) + 2\pi i(\nu_j - \nu) \quad (3)$$

$T_2^*(j)$ is the line width parameter in the absence of exchange. The doublets 1 and 4 carry an index + or - to indicate the spin of the added proton.

In the limit of slow exchange the broadening of lines 1 and 4 is given by

$$1/T_2(1) = 1/T_2^*(1) + \tau_{13}^{-1} \quad (4)$$

$$1/T_2(4) = 1/T_2^*(4) + \tau_{42}^{-1} \quad (5)$$

i.e. τ_{13} and τ_{42} are equal to the lifetime of the proton complex τ .

For the broadening of lines 2 and 3 (the *o*- and *m*-methyl groups):

$$1/T_2(2) = 1/T_2^*(2) + (\tau_{23}^{-1} + \tau_{24}^{-1}) \quad (6)$$

$$1/T_2(3) = 1/T_2^*(3) + (\tau_{31}^{-1} + \tau_{32}^{-1}) \quad (7)$$

Evidently

$$\tau_{23}^{-1} = \tau_{24}^{-1} = \tau_{31}^{-1} = \tau_{32}^{-1} = 1/2 \tau^{-1} \quad (8)$$

ISOTOPE EFFECT IN HEXAMETHYLBENZENE

The equations (2) can be written in the slow-passage approximation:

$$(\alpha_1 + \tau + 1)G_1^+ - 1/2 G_3 = -i\gamma H_1 M_0 \tau/6 \quad (9a)$$

$$-(\alpha_2 + \tau + 1)G_2 - 1/2 G_3 - G_4^+ = -i\gamma H_1 M_0 \tau/3 \quad (9b)$$

$$- G_1^+ - 1/2 G_2 + (\alpha_3 + \tau + 1)G_3 = -i\gamma H_1 M_0 \tau/3 \quad (9c)$$

$$- 1/2 G_2 + (\alpha_4 + \tau + 1)G_4^+ = -i\gamma H_1 M_0 \tau/6 \quad (9d)$$

The imaginary part of $\sum_{i=1}^4 G_i^+$ was calculated with the aid of an analogon computer. The line width $T_2^*(i)$ in the absence of exchange was taken to be 1.5 c/s except for the *o*-methyl signal where it was taken twice as large in order to account for the unresolved spin coupling with the added proton. The line shapes are determined by the product $\tau^{-1} T_2^*$. Figure 3 gives the absorption mode of $\sum_{i=1}^4 (G_i^+ + G_i^-)$ for a number of values of the parameter $\tau^{-1} T_2^*$.

The analysis of the rates in our experiments is predominantly based on a comparison of the measured spectra with the calculated ones. The spectra were measured at temperature intervals of a few degrees and values of the parameter ($\tau^{-1} T_2^*$) could be obtained with an estimated probable error of about 20 per cent. The results of the analogon computer calculations should in the limits of slow and rapid exchange coincide with analytical expressions which we will now discuss.

At low temperatures (Figures 1(a) and (b)) the lines are narrow and their overlap is small so that the slow exchange approximation (equations 5-8) can be used. In order to obtain a reliable value of τ^{-1} the line width in the absence of exchange should be as small as possible. The *p*- and *o*-methyl groups are broadened by spin coupling and for this reason the *m*-methyl peak is especially suitable for determining the rate: at the lowest temperatures it has a width of 2.0 c/s.

In the limit of fast exchange (Figures 2(a) and (b)) one can relate the line width of the collapsed line to the life time of the ion. The determinant Δ of equations (9) determines the line shape, provided τ is so short that the quadratic terms in τ can be neglected unless they appear multiplied by large factors such as $\alpha_i \alpha_j$. Then the determinant is given by:

$$\Delta = 3/2 \tau(1/6 \alpha_1 + 1/3 \alpha_2 + 1/3 \alpha_3 + 1/6 \alpha_4) + 3/2 \tau^2 \\ [2/3 (\alpha_1 \alpha_2 + \alpha_2 \alpha_3 + \alpha_3 \alpha_4) + 1/3 (\alpha_1 \alpha_3 + \alpha_1 \alpha_4 + \alpha_2 \alpha_4)]$$

The indices + or - for α_1 and α_4 have been dropped, which means that the spin splittings are neglected.

When the exchange is so fast that it no longer broadens the collapsed line the shape is determined by the first term; the width then is:

$$1/T_2 = 1/6 T_2^*(1) + 1/3 T_2^*(2) + 1/3 T_2^*(3) + 1/6 T_2^*(4) \quad (10)$$

and the line is centred at

$$\omega = 1/6 \omega_1 + 1/3 \omega_2 + 1/3 \omega_3 + 1/6 \omega_4 \quad (11)$$

In the next approximation we keep the real part of the second term. Neglecting products $\{T_2^*(i) T_2^*(j)\}^{-1}$ the real part of this term reads:

$$-\tau/3 [2\{(\omega_2 - \omega)(\omega_1 - \omega) + (\omega_3 - \omega)(\omega_2 - \omega) + (\omega_4 - \omega)(\omega_3 - \omega)\} + \{(\omega_3 - \omega)(\omega_1 - \omega) + (\omega_4 - \omega)(\omega_1 - \omega) + (\omega_4 - \omega)(\omega_2 - \omega)\}]$$

After inserting the shifts of the lines at 60 MHz we find the correction in the transverse relaxation time T_2 :

$$1/T_2 = 1/T_2^* + 24,000\tau \quad (12)$$

where τ is the lifetime of the ion. The second moment of the methyl lines $\nabla = \sum_i p_i(\omega_i - \omega)^2$ is 24,000, so that as expected⁶

$$1/T_2 = 1/T_2^* + \tau\nabla \quad (13)$$

The region of $\tau^{-1} T_2^*$ values in which this formula is valid can be found from the analogon computer calculations as the results of these should coincide with those obtained from equation (13) at high rates of exchange.

In deuterium fluoride one would in principle expect each doublet splitting to become a set of three lines owing to spin coupling of the methyl hydrogens with the added deuterium. The spectrum of *Figure 1(b)* does not show this triplet splitting. It cannot be decided with certainty that the triplet splitting is absent owing to a short relaxation time of the deuterium: the splitting between adjacent lines (1 c/s) is so small that it may easily be masked by field inhomogeneities. Equation (13) should, therefore, in good approximation be valid for the high-temperature spectra of the methyl groups if measured in DF. The corresponding spectrum in HF, on the other hand, is a doublet (2.1 c/s) resulting from the two different spin states of the added proton. These lines overlap considerably and the correction T_2^* of equation (13) depends on the rate of exchange. The correction was calculated by superposing two identical Lorentzian lines of varying widths, separated by 2.1 c/s.

RESULTS

The methods of the previous sections were applied to obtain the rates of transfer in HF and DF of the proton (deuteron) in hexamethylbenzene carbonium ion. *Figure 4*, curves *a* and *b* represent the data

$$k_H = \frac{kT}{h} e^{3.9/R} e^{-11,300/RT} \quad (14)$$

$$k_D = \frac{kT}{h} e^{8.8/R} e^{-13,000/RT} \quad (15)$$

The activation energy (estimated uncertainty: 800 cal/mole) is somewhat higher than previously reported³. The difference is mainly caused by slightly lower rates measured in the last series of experiments at the low temperatures. For this difference two causes can be given, firstly, it has proved more difficult than expected to get accurate temperature readings in the variable-temperature probe, and secondly small but significant differences in the width of n.m.r. lines were observed in freshly prepared and

ISOTOPE EFFECT IN HEXAMETHYLBENZENE

older solutions. As mentioned above, there is a slow change of colour from pale yellow to brown, which may be caused by the photochemical formation of the hexamethylbenzene radical ion⁷. Such paramagnetic impurities will broaden n.m.r. lines. Initially this discoloration was even more severe in DF which apparently contained traces of an oxidizing substance.

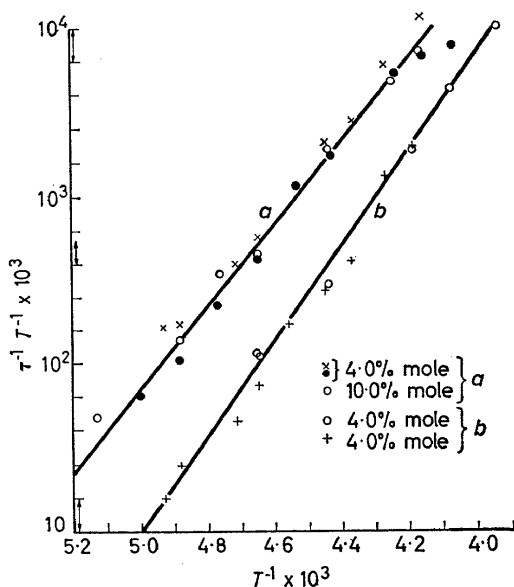


Figure 4. Rate plot of (a) proton and (b) deuteron transfer reaction; the double arrows at the left indicate the margin of error of the rates

The ideal experiment would, of course, be to determine the isotope effect of the exchange rates in a combined solvent *i.e.* a mixture of HF and DF. Unfortunately, the overlap of the signals of the methyl groups for the deuterated and the protonated species prohibits an accurate measurement of the isotope effect (see Figure 5). However, at the low or high temperatures a reliable estimate of the rate of exchange of $(\text{HMB})\cdot\text{D}^+$ or $(\text{HMB})\cdot\text{H}^+$, respectively, could be obtained.

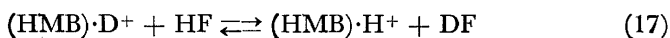
For the determination of the isotope effect in another series of experiments the spectra of HF and DF solutions were measured one after the other, the thermocouple reading being kept constant and the temperature being equilibrated for each sample for one hour (see Table 1). These results can be represented by

$$k_{\text{H}}/k_{\text{D}} = 0.35 e^{+1200/RT} \quad (16)$$

Within the experimental error equation (16) is in agreement with equations (14) and (15).

Additional points which have a bearing on the interpretation and accuracy of the experiment are the following.

The equilibrium isotope effect of the reaction



with

$$K = [(\text{HMB})\cdot\text{H}^+] [\text{DF}] / [(\text{HMB})\cdot\text{D}^+] [\text{HF}]$$

was found to be little different from unity:

$$K = 1.2 \pm 0.2 (-78^\circ)$$

and

$$K = 1.5 \pm 0.2 (+23^\circ)$$

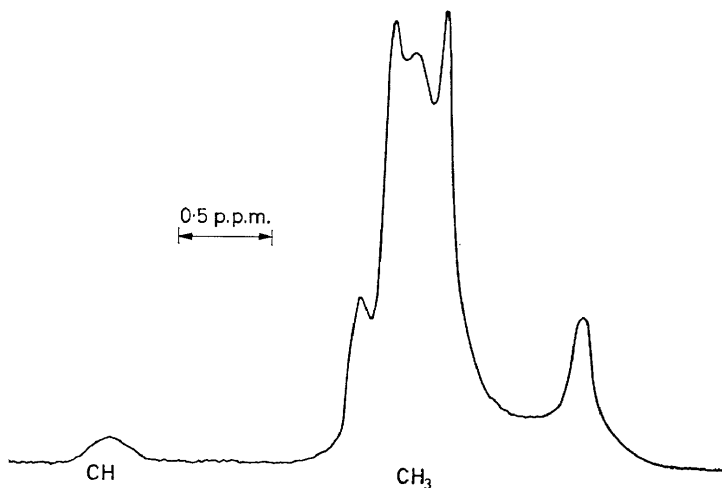


Figure 5. The n.m.r. spectrum of hexamethylbenzene in HF/DF (50:50) + BF_3 at -60° ; field increasing from left to right; scale as indicated

K was determined in a 50/50 HF/DF mixture by integrating the n.m.r. signals of the CH and the CH_3 groups.

The reaction seems to be little affected by the concentration of the base or by the type of counter ion present (BF_4^- , PF_6^-). The differences between

Table 1. Rates of exchange in 4 mole per cent solutions of hexamethylbenzene in HF and DF (see text)

Temperature ($^\circ\text{C}$)	τ_{H}^{-1} (sec^{-1})	τ_{D}^{-1} (sec^{-1})	$k_{\text{H}}/k_{\text{D}}$	$T^{-1} \times 10^3$
-33	2800			} 4.18
-34		460	5.7	
-39	1390	320	4.3	4.28
-44	750	94	7.9	4.37
-49			7.8	4.45
-53 ^s	350	37	9.5	4.56
-58	120	16	7.5	4.65
-61	85	9 ^s	9.1	4.71 ^s
-68	36	$3.5 < \tau^{-1} < 5$	$7-10^5$	4.88
-71	33	$2 < \tau^{-1} < 3$	< 10	4.93

ISOTOPE EFFECT IN HEXAMETHYLBENZENE

the rates measured in HF/BF_3 for solutions containing 3.8 and 10 mole per cent HMB (see *Figure 4*) are within the experimental error.

The temperature readings below about -40° in the Varian variable-temperature Dewar insert have to be calibrated. The sample temperature is higher than is indicated by the thermocouple and corrections may amount to four degrees. A replacement of the thermocouple may cause the temperature calibration to change. We finally calibrated the temperature scale using the temperature dependence of the chemical shifts in methanol as suggested by Varian for their A60 spectrometers (V6040-n.m.r. temperature controller). Further check points were the melting points of benzene and chloroform. The accuracy of the rate determinations is estimated as follows. When the rate is obtained from the broadening of a single line, as is the case in the low- and high-temperature regions, the accuracy is limited by the uncertainty of the linewidth in the absence of exchange. The latter is 1.5 ± 0.5 c/s. In the intermediate range the parameter ($\tau^{-1} T_2^*$) is obtained by comparing the experimental spectra with the calculated ones. The accuracy in this case is estimated to be 20 per cent. The magnitudes of the uncertainties in the rates have been indicated in the vertical scale of *Figure 4*. The estimated uncertainty in the temperature is $\pm 1^\circ$ at the lowest temperature and becomes smaller at higher temperatures.

The structures of the proton complex of hexamethylbenzene and of the transition state

From the n.m.r. and other spectroscopic data the following picture of the structure of the hexamethylbenzene proton complex emerges.

(a) The proton is attached to a carbon atom of the nucleus, thereby forming a $\begin{array}{c} \text{H} \\ \diagup \text{C} \diagdown \\ \text{CH}_3 \end{array}$ group, which is aliphatic in nature². If—as in pentamethylbenzene—an unsubstituted carbon atom is present, that atom is substituted with formation of a $\begin{array}{c} \text{H} \\ \diagup \text{C} \diagdown \\ \text{CH}_2 \end{array}$ group (see *Figure 6*).

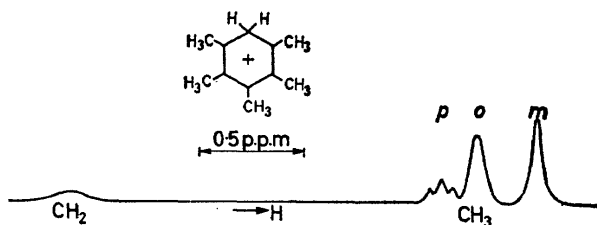


Figure 6. The n.m.r. spectrum at 60 Mc/s of pentamethylbenzene in $\text{HF}\cdot\text{BF}_3$ at -60° ; field increasing from left to right; scale as indicated

(b) The $\begin{array}{c} \text{H} \\ \diagup \text{C} \diagdown \\ \text{CH}_3 \end{array}$ group (or $\begin{array}{c} \text{H} \\ \diagup \text{C} \diagdown \\ \text{CH}_2 \end{array}$ in pentamethylbenzene) is bonded to, and interacts fairly strongly with, the remaining conjugated pentadienyl

system⁸. This is reflected, for instance, in the existence of a surprisingly large long-range spin-spin coupling between the aliphatic proton of the >CHCH_3 (or >CH_2) group and the methyl hydrogens in *p*-position. There is a considerable difference between the coupling constants of the carbonium ions of hexa- and pentamethylbenzene: 2 c/s and 3.5 c/s respectively. According to the theory of these couplings^{8, 9}, the methylenic hydrogen in >CHCH_3 should be nearer the plane of the ion than it is in the CH_2 group of pentamethylbenzenium ion, and consequently the CH_3 is fairly far out of the plane. The steric strain in hexamethylbenzene is relieved in this manner, it seems.

(c) The proof that the transfer reaction responsible for the collapse of the spectrum is intramolecular is furnished by the high temperature spectrum in hydrogen fluoride (*Figure 2(a)*). The multiplet structure of the CH group is in accordance with a proton coupled to one of the 19 possible spin states of the 18 methyl hydrogens. Actually in the best spectra 13 to 15 of the 19 lines can be recognized. Likewise the doublet of the methyl hydrogens demonstrates the persistence of the spin state of the added proton. Neither multiplet would exist if the reaction were bimolecular. There is additional evidence to support this conclusion. The proton complex of pentamethylbenzene, a somewhat weaker base, displays a sharp spectrum at room temperature in HF/BF_3 (*Figure 6*); there is neither bimolecular nor intramolecular transfer.

(d) The mobile bond orders between the carbon atoms of the conjugated pentadienyl system are high and the bond lengths must be correspondingly small (1.40 Å). The bonds leading to the >CHCH_3 group are more aliphatic in nature and as a consequence much longer (about 1.50 Å).

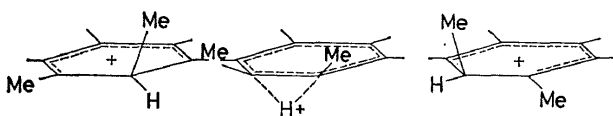


Figure 7. Model of the transfer reaction

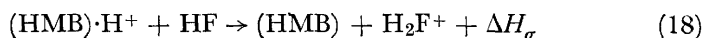
During its transfer from one carbon atom to the next the proton will go through a symmetric, probably π -bonded position between the two carbon atoms (*Figure 7*). It is unlikely that the proton should jump between carbon atoms in *meta* position since protonated mesitylene does not transfer its proton intramolecularly³.

DISCUSSION

The transfer of the proton between two adjacent carbon atoms of the nucleus of protonated hexamethylbenzene requires considerable activation (12 kcal/mole) and has a surprisingly high frequency factor ($\sim 10^{14}$).

ISOTOPE EFFECT IN HEXAMETHYLBENZENE

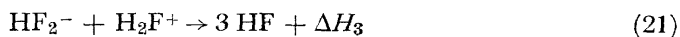
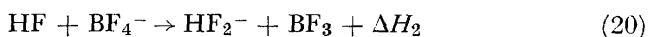
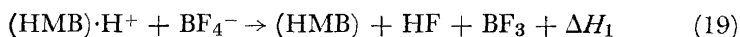
In order to test more quantitatively the model of *Figure 7*, it would be of interest to estimate the amount of bonding in the π -complexed transition state. One first of all would like to determine the enthalpy ΔH_σ of



which is directly related to the energy of the stable σ complex. ΔH_σ is related by

$$\Delta H_\sigma = \Delta H_1 - \Delta H_2 - \Delta H_3$$

to the enthalpies of the following reactions



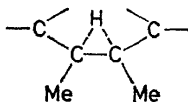
Values of $\Delta H_1 \sim 16$ kcal/mole and $\Delta H_2 = 11.3$ kcal/mole have been determined¹⁰, but little is known about ΔH_3 . An estimation of the value of the self-ionization constant of HF indicates that it is of the same order of magnitude as that of water¹⁰ or even smaller. We will assume the ionization energies for H_2O and HF to be about equal; thus, $-\Delta H_3 \sim 10$ kcal/mole and $\Delta H_\sigma \sim 15$ kcal/mole.

In terms of the transition state theory, the π -bonded transition state is ~ 12 kcal/mole higher in energy than the σ complex; the enthalpy ΔH_π defined similarly to ΔH_σ in reaction (18) would be: $\Delta H_\pi = 3$ kcal/mole. This may mean that in the transition state only a loose complex between the added proton and hexamethylbenzene exists. Actually the molecule in the transition state might be only little distorted from the regular hexagon and the aliphatic CH bond in the σ -complexed carbonium ion between proton and carbon atom has now become weak. For such a situation the difference in activation energy for the two isotopes is expected to be of the order of the zero-point energy differences for CH and CD bonds which is 1.15 kcal/mole, in agreement with the experimental result [cf. equation (16)].

The discussion of the isotopic differences in the frequency factor is much more difficult¹¹. As pointed out above, the transfer of the proton is a complicated process during which there are also considerable displacements of methyl groups as well as changes in length of the carbon-carbon bonds of the nucleus. The transfer of the proton along the reaction coordinate is, therefore, most likely to be coupled with the out-of-plane modes of the methyl groups and the stretching modes of the carbon-carbon bonds of the nucleus. It is expected that the mass of the particle along the reaction coordinate will exceed that of the mass of the proton considerably, which will tend to make the measured isotope effect smaller.

The proper manner to tackle this problem is by making calculations of the vibrational frequencies using the FG-matrix method of Wilson, Decius and Cross^{12, 13}. We are currently making calculations, in co-operation with

Dr P. Cossee of this laboratory, on a model with seven or more mass points representing *e.g.* the following fragment of the ion:



The experimental assistance of Messrs F. J. Reinders and J. Gaaf is gratefully acknowledged.

References

- ^{1a} D. A. McCaulay and A. P. Lien. *J. Am. Chem. Soc.* **73**, 2013 (1951).
- ^b M. Kilpatrick and F. E. Luborsky. *J. Am. Chem. Soc.* **75**, 577 (1953).
- ^c E. L. Mackor, A. Hofstra, and J. H. van der Waals. *Trans. Faraday Soc.* **54**, 186 (1958).
- ² C. MacLean, J. H. van der Waals, and E. L. Mackor. *Mol. Phys.* **1**, 247 (1958).
C. MacLean and E. L. Mackor. *Mol. Phys.* **4**, 241 (1961).
- ³ C. MacLean and E. L. Mackor. *Discussions Faraday Soc.* **34**, 165, 201 (1962).
- ⁴ G. Oláh and S. Kuhn. *Z. Anorg. Allgem. Chem.* **282**, 287 (1956).
- ⁵ H. S. Gutowsky, D. W. McCall, and C. P. Slichter. *J. Chem. Phys.* **21**, 279 (1953).
H. M. McConnell. *J. Chem. Phys.* **28**, 430 (1958).
- ⁶ L. H. Piette and W. A. Anderson. *J. Chem. Phys.* **30**, 899 (1959).
- ⁷ R. Hulme and M. C. R. Symons. *Proc. Chem. Soc.* **1963**, 241.
- ⁸ J. P. Colpa, C. MacLean, and E. L. Mackor. *Tetrahedron* **19**, 84 (1963).
- ⁹ M. Karplus. *J. Chem. Phys.* **33**, 1842 (1960);
H. M. McConnell. *J. Mol. Spectr.* **1**, 11 (1957).
- ¹⁰ C. MacLean and E. L. Mackor. *Proc. Colloque Ampère*, Eindhoven 1962, p. 571, North-Holland, Amsterdam (1960).
- ¹¹ R. P. Bell. *The Proton in Chemistry*, Chapter XI, Methuen, London (1959).
- ¹² E. B. Wilson Jr., J. C. Decius, and P. C. Cross. *Molecular Vibrations*, McGraw-Hill, New York (1955).
- ¹³ See for instance, H. S. Johnston. *Advan. Chem. Phys.* **3**, 131 (1961);
M. Wolfberg and M. J. Stern. *Pure Appl. Chem.* **8**, 225 (1964).