

Table VII. Contributions of Various Types of Motions to the Ratios k_H/k_T^a

T (K)	η_{tun}	η_{rot}	$\eta_{\text{vib,in}}$	$\eta_{\text{vib,out}}$	$\eta_{\text{vib,bb}}$
200	0.55	1.01	35.44	0.42	1.54
300	0.77	1.01	10.85	0.58	1.38
500	0.91	1.01	4.26	0.75	1.30

^a $\eta_{\text{vib,in}}$ is from in-plane hydrogenic stretch and bend vibrational modes. $\eta_{\text{vib,out}}$ is from the out-of-plane hydrogenic bend vibrational mode. $\eta_{\text{vib,bb}}$ is from the remaining backbone vibrational modes.

mostly the backbone heavy atom motions. These individual contributions can be calculated by using eq 7 for selected mode(s).

The resulting contributions to the ratios of k_H/k_T are given in Table VII. First of all, the rotational motions, as expected, have little effect on the KIE; i.e., η_{rot} is near unity for the entire temperature range. As discussed earlier, tunneling decreases the KIE; in particular, η_{tun} decreases from 0.91 to 0.55 as the temperature decreases from 500 to 200 K. For the vibrational motions, the out-of-plane hydrogenic bend mode is found to decrease the KIE. This is probably due to the fact the hydrogen out-of-plane bend mode is tighter at the transition state than at the reactant. Interestingly, we found that the hydrogenic in-plane modes are mostly responsible for the large KIE observed in this reaction. $\eta_{\text{vib,in}}$ increases from 4.26 to 35.44 as the temperature decreases from 500 to 200 K. The remaining backbone modes account for a 30–60% increase in the KIE for the temperature range from 200 to 500 K.

It is important to point out that there are some limitations in the present calculations. First of all, recrossing effects are not included in this study. Such effects would lower the calculated transfer rates, and might be important for double well potentials with low barriers such as those considered here. For proton transfer in the hydrogenoxalate anion, one might expect the recrossing effect to be larger for the proton than for its heavier isotopes, since it has the smallest effective barrier. Consequently,

it would lower the calculated KIE somewhat. Finally, the anharmonicity effects were not included in calculating the vibrational partition functions and zero-point energies in the present calculations. Such effects might be nonnegligible for low-frequency modes.

4. Conclusion

We have carried out ab initio calculations for the intramolecular proton transfer in the hydrogenoxalate anion. We found that electron correlation, especially from d orbitals on the heavy atoms, is quite important in predicting the barrier height and the structures of both the reactant and transition state. The classical barrier height for this process calculated at the MP2/6-31++G** level is 3.1 kcal/mol as compared to the order of 9–10 kcal/mol at the HF level. Including the zero-point energy correction calculated at the HF/6-31++G** level reduces the barrier to only 0.4 kcal/mol for proton transfer, and to 1.3 and 1.6 kcal/mol for deuteron and triton transfer, respectively.

The rate constants and KIE for the intramolecular proton-transfer process are calculated by using transition-state theory plus the semiclassical zero-curvature ground-state tunneling method. Due to the small effective barrier, we found that the tunneling contribution to the rate constants is small for this proton-transfer reaction. Despite the effect of tunneling, the KIE is still anomalously large due mainly to the in-plane hydrogenic stretch and bend vibrational modes.

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Vibrational Stabilization of Preferred Conformations of Partially Deuterated *n*-Butane Cations: Comparison of ab Initio Calculations and Electron Spin Resonance Results

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Abstract: The role of the zero-point vibrational energy (ZPE) in determining the preferred conformations of partially deuterated *n*-butane cations has been studied, using ab initio UHF/6-31G** and MP2/6-31G* calculations. By comparison with matrix isolation electron spin resonance (ESR) measurements, it is found that the experimental spectra at 77 K are fully explained by assuming a Boltzmann distribution over the nine possible rotational isomers related by rotations of the terminal methyl groups. The spectrum at 4 K, however, corresponds to the equilibrium distribution at a considerably higher temperature, 40–50 K, indicating that equilibration through rotational rearrangement is hindered at temperatures lower than this. In addition, hyperfine coupling constants, obtained from configuration interaction (SDCI) calculations, are reported and compared with experiment.

The use of selective deuteration in electron spin resonance (ESR) experiments has proven to be a powerful technique to investigate the structure of hydrocarbon radical cations, by distinguishing groups of chemically inequivalent protons.¹ Upon

ionization, however, distortions often occur, which cause protons which are chemically equivalent in the un-ionized molecule to become structurally inequivalent in the cation. This is obvious

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(1) For a recent review, see: Shiotani, M.; Lund, A. In *Radical Ionic Systems*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, 1991; pp 151–176.

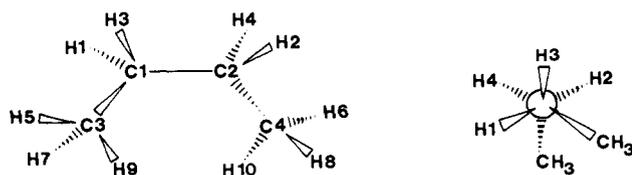


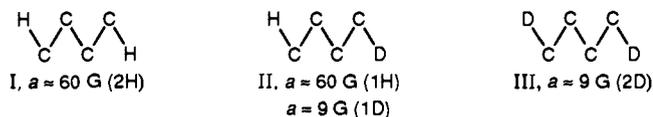
Figure 1. Geometry of the *n*-butane cation (here shown in its gauche conformation), showing the labeling used in Tables I–VI.

when the ion is Jahn–Teller unstable, like CH_4^{+2} or $\text{C}_2\text{H}_6^{+1,3}$ but may occur also in other cases, such as $\text{C}_3\text{H}_8^{+4,5}$ and $\text{C}_4\text{H}_{10}^{+6}$. Since the D-labeling is done in the parent compound prior to ionization, it does not directly provide information about these effects.

By going to low enough temperatures, however, it is possible to exploit the difference in vibrational properties between protons and deuterons. Since the zero-point energy (ZPE) of, e.g., a C–H stretching vibration to a first approximation is proportional to $(k/m)^{1/2}$, k being the force constant and m the mass of the hydrogen nucleus, the decrease in ZPE upon deuteration will be larger for bonds having higher force constants. This, in turn, implies that the deuterium atoms will preferentially occupy such binding sites at low temperatures. As an example, Knight et al.² succeeded in obtaining conclusive experimental evidence for a C_{2v} ground state of the CH_2D_2^+ cation, the two short bonds being occupied by deuterium atoms and the two longer bonds by protons, by lowering the temperature to 4.2 K. Careful theoretical analyses of the vibrational motion, confirming the original interpretation, have subsequently been performed by Paddon-Row et al.⁷ and Frey and Davidson.⁸

Partially D-labeled *n*-butane cations have been studied by matrix isolation ESR experiments by Lindgren et al.^{9,10} at 4.2 K, 77 K, and above 90 K, using CF_3CCl_3 as a matrix. The dominant hyperfine couplings could be assigned to the “in-plane” hydrogens H5 and H6 in the terminal methyl groups, the planes in question being defined by (H5)–C3–C1–C2 and C1–C2–C4(–H6), respectively (cf. Figure 1). In the original papers,^{9,10} it was suggested that the cation is observed in the gauche conformation rather than the trans conformation which has the lower energy in the gas phase. It should, however, be mentioned that an alternative interpretation in terms of the trans conformation has been advocated by Iwasaki and co-workers^{11,12} (see Discussion).

Considering, e.g., *n*-butane-1,1,4,4- d_4 and displaying only the atoms in the two above-mentioned planes, i.e., H5–C3–C1–C2–C4–H6, rotational isomers I–III, related by internal rotations of



the terminal methyl groups, are possible, with the appropriate (experimental) coupling constants indicated.^{9,10}

(2) Knight, L. B., Jr.; Steadman, J.; Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 3700.

(3) Lunell, S.; Huang, M.-B. *J. Chem. Soc., Chem. Commun.* **1989**, 1031. Huang, M.-B.; Lunell, S. *Chem. Phys.* **1990**, *147*, 85.

(4) Lunell, S.; Huang, M.-B.; Lund, A. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 35.

(5) Lunell, S.; Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1990**, *77*, 111.

(6) Huang, M.-B.; Lunell, S. *J. Mol. Struct. (THEOCHEM)* **1990**, *205*, 317.

(7) Paddon-Row, M. N.; Fox, D. J.; Pople, J. A.; Houk, K. N.; Pratt, D. W. *J. Am. Chem. Soc.* **1985**, *107*, 7697.

(8) Frey, R. F.; Davidson, E. R. *J. Chem. Phys.* **1988**, *88*, 1775.

(9) Lindgren, M.; Lund, A.; Dolivo, G. *Chem. Phys.* **1985**, *99*, 103.

(10) Lindgren, M.; Lund, A. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1815.

(11) Iwasaki, M.; Toriyama, K. *J. Am. Chem. Soc.* **1986**, *108*, 6441.

(12) Matsuura, K.; Nunome, K.; Toriyama, K.; Iwasaki, M. *J. Phys. Chem.* **1989**, *93*, 149.

Table I. HF/6-31G** and MP2/6-31G* Optimized Geometries for the Gauche and Trans Conformations of the *n*-Butane Cation^a

	gauche		trans	
	HF/ 6-31G**	MP2/ 6-31G*	HF/ 6-31G**	MP2/ 6-31G*
R(C1–C2)	2.0031	1.9112	1.9923	1.8995
R(C1–C3)	1.4859	1.4716	1.4869	1.4734
R(C1–H1)	1.0780	1.0897	1.0779	1.0894
R(C1–H3)	1.0777	1.0901	1.0779	1.0894
R(C3–H5)	1.0932	1.1091	1.0932	1.1095
R(C3–H7)	1.0806	1.0892	1.0818	1.0905
R(C3–H9)	1.0819	1.0914	1.0818	1.0905
∠(C1–C2–C4)	108.7	108.7	107.5	106.5
∠(H1–C1–C2)	95.1	96.9	95.5	97.5
∠(H3–C1–C2)	94.8	95.5	95.5	97.5
∠(H5–C3–C1)	104.9	103.5	105.2	103.4
∠(H7–C3–C1)	113.1	114.0	112.9	113.9
∠(H9–C3–C1)	112.8	113.7	112.9	113.9
∠(C3–C1–C2–C4)	66.6	62.4	180.0	180.0
∠(H5–C3–C1–C2)	177.7	172.3	180.0	180.0
E_{UHF}	–156.97266		–156.97346	
E_{MP2}		–157.46829		–157.46882
(S^2)	0.7579	0.7510	0.7579	0.7510
E_{SDCI}^b		–157.46339		–157.51601
no. of spin- adapted conf.		51 496		53 350

^aDistances are in angstroms, angles in degrees, and energies in atomic units (1 au = 2627.3 kJ/mol). ^bSDCI results obtained using the [5s,4p,1d]/[4s,1p] basis.

The ESR spectrum of this cation at 77 K could not, however, be explained by any single one of these isomers.⁹ This can be taken as an indication that the temperature is not low enough to single out one particular conformation as a unique ground state. A superposition of the simulated spectra of the rotational isomers I, II, and III in the statistically expected ratio 1 : 4 : 4 also agrees poorly with experiment. Instead, a superposition in the ratio 3 : 5 : 2 (more exactly, 3.0 : 4.9 : 2.1) of the spectra corresponding to the isomers I, II, and III, respectively, was found to closely simulate the observed spectrum, with regard to both its intensity distribution and the hyperfine pattern associated to a partially D-labeled gauche structure.⁹ In a later publication, the same authors extended this study to the *n*-butane-1,4- d_2 cation at several temperatures, from 4.2 K to 122 K.¹⁰ Also in this case, strong deviations from the statistically expected population ratios had to be assumed, in order to achieve a satisfactory agreement between observed and simulated spectra.

The purpose of the present work is to investigate to what extent these empirical results can be explained and predicted from differences in vibrational energy between the rotational isomers arising from rotations of the terminal methyl groups. We have therefore calculated the zero-point vibrational energy for the *n*-butane-1,1,4,4- d_4 and *n*-butane-1,4- d_2 cations by quantum chemical ab initio methods, for each of the nine different isomers of both the gauche and trans forms, and studied the thermal distribution over the different isomers. In addition, configuration interaction calculations including single and double excitations (SDCI) have been used to obtain proton hyperfine coupling constants, which are compared with the experimental ones.

Method

The equilibrium geometries of the trans and gauche conformations of the *n*-butane cation have in an earlier paper been determined at the UHF/3-21G and UHF/3-21G* levels of approximation.⁶ In the present work, these geometry optimizations were extended to the UHF/6-31G** and MP2/6-31G* levels. In order to verify that the MP2 equilibrium geometry is not qualitatively changed by the inclusion of polarization functions on the hydrogens, as has previously been found to be the case for the ethane cation,³ limited geometry searches around certain critical values of the C–C bond lengths were performed also at the MP2/6-31G** level. These geometry searches, however, tended toward a geometry very close to the MP2/6-31G* one. The importance of hydrogen atom polarization functions was therefore judged to be only marginal, as in, e.g., the propane cation,⁵ and complete MP2/6-31G** optimizations were therefore not performed. Vibrational frequencies and zero-point energies were calculated at the UHF/3-21G and UHF/6-31G** levels. The geometry optimizations utilized the program GAUSSIAN 86¹³

Table II. Calculated (HF/6-31G**) Zero-Point Vibrational Energies and Boltzmann Populations for the Different Rotational Isomers of the *n*-Butane-1,1,4,4-*d*₄ Cation (HF/3-21G Results in Parentheses)

undeuterated positions	statistical weight	ZPE energy, kJ/mol	$\exp[(E - E_0)/RT]$, $T = 77$ K	rotational isomer
A. Trans Conformation				
5, 6	1	320.032	1.0000	I
5, 8 [5, 10; 6, 7; 6, 9]	4	320.461	0.5116	II
7, 8 [9, 10]	2	320.981	0.2271	III
7, 10 [8, 9]	2	321.014	0.2157	III
B. Gauche Conformation				
5, 6	1	320.190 (323.028)	1.0000 (1.0000)	I
5, 8 [6, 7]	2	320.776 (323.306)	0.4004 (0.6477)	II
5, 10 [6, 9]	2	320.744 (323.273)	0.4209 (0.6820)	II
7, 8	1	321.308 (324.103)	0.1744 (0.1865)	III
7, 10 [8, 9]	2	321.180 (323.811)	0.2130 (0.2943)	III
9, 10	1	321.145 (323.679)	0.2250 (0.3617)	III

Table III. Calculated (HF/6-31G**) and Observed Abundance Ratios of the Rotational Isomers I-III of the *n*-Butane-1,1,4,4-*d*₄ Cation at 77 K (HF/3-21G Results in Parentheses)

	rotational isomer		
	I	II	III
A. Trans Conformation			
statistical abundance ratio	1	4	4
calculated Boltzmann population	1	2.0466	0.8855
calculated abundance ratio	2.5	5.2	2.3
B. Gauche Conformation			
statistical abundance ratio	1	4	4
calculated Boltzmann population	1 (1)	1.6426 (2.6594)	0.8254 (1.1368)
calculated abundance ratio	2.9 (2.1)	4.7 (5.5)	2.4 (2.4)
experimental abundance ratio ^a	3.0	4.9	2.1

^aReference 9; observed in CF₃CCl₃.

and its analytic gradient routines, while the frequencies were calculated numerically from analytical first derivatives, using the GAMESS¹⁴ program system. C₂ symmetry was assumed throughout (C_{2h} for the trans conformation).

Hyperfine coupling constants (hcc) were obtained from SDCI calculations including approximately 50 000 configurations, for which the program MELDF¹⁵ was used. The uncontracted basis sets were for carbon the (13s, 8p) basis and for hydrogen the (10s) basis given by van Duijneveldt,¹⁶ on the one hand, contracted to [5s, 3p] and [4s], respectively, and, on the other hand, contracted to [5s, 4p]/[4s] and augmented with 3d (0.75) polarization functions on the carbons and 2p (1.0) polarization functions on the hydrogens. All single excitations out of a RHF reference determinant were included in the CI, plus the most important double excitations as selected by second-order perturbation theory.¹⁷ Before CI, the orbitals were transformed to so-called K orbitals,¹⁸ which are approximate frozen natural orbitals, in order to improve the CI convergence.

Results

The MP2/6-31G* and HF/6-31G** optimized geometries of the gauche and trans forms of the *n*-butane cation are given in Table I. In the present context, the most interesting parameters are the C-H bond lengths in the terminal methyl groups, which for the gauche conformation were obtained as 1.109 (1.093) Å for the in-plane hydrogens H5 and H6, and 1.089 (1.081) Å and 1.091 (1.082) Å, respectively, for the out-of-plane hydrogens H7-H10 (HF/6-31G** results within parentheses). The corresponding values for the trans conformation are 1.110 (1.093), 1.090 (1.082), and 1.090 (1.082), respectively.

(13) GAUSSIAN 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghuvaran, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A.; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

(14) Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog, Vol. 1, Program QG01 (GAMESS), 1980, as modified by M. W. Schmidt and S. T. Elbert.

(15) The MELDF suite of programs was developed by E. R. Davidson and co-workers, Indiana University, Bloomington, IN.

(16) van Duijneveldt, F. B. IBM Technical Report RJ945, 1971.

(17) Davidson, E. R. and Bender, C. F. *Chem. Phys. Lett.* **1978**, *59*, 369.

(18) Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3977.

Table IV. Calculated (HF/6-31G**) Zero-Point Vibrational Energies and Boltzmann Populations for the Different Rotational Isomers of the *n*-Butane-1,4-*d*₂ Cation at 77 K

deuterated positions	statistical weight	ZPE energy, kJ/mol	$\exp[(E - E_0)/RT]$, $T = 77$ K	rotational isomer
A. Trans Conformation				
5, 6	1	339.032	0.2110	III
5, 8 [5, 10; 6, 7; 6, 9]	4	338.599	0.4150	II
7, 8 [9, 10]	2	338.069	0.9498	I
7, 10 [8, 9]	2	338.036	1.0000	I
B. Gauche Conformation				
5, 6	1	339.297	0.1690	III
5, 8 [6, 7]	2	338.700	0.4295	II
5, 10 [6, 9]	2	338.736	0.4060	II
7, 8	1	338.159	1.0000	I
7, 10 [8, 9]	2	338.295	0.8086	I
9, 10	1	338.330	0.7656	I

Table V. Calculated (HF/6-31G**) and Observed Abundance Ratios of the Rotational Isomers I-III of the *n*-Butane-1,4-*d*₂ Cation

	temp, K	rotational isomer		
		I	II	III
A. Trans Conformation				
statistical abundance ratio		4	4	1
calculated abundance ratio	77	6.8	2.9	0.4
B. Gauche Conformation				
statistical abundance ratio		4	4	1
calculated abundance ratio	77	6.5	3.2	0.3
	50	7.4	2.5	0.1
	45	7.6	2.3	0.1
	40	7.9	2.0	0.1
	30	9.4	0.6	0.0
	4	10.0	0.0	0.0
experimental abundance ratio	77 ^a	6	3	(1) ^b
	4 ^c	7	2	

^aReference 10; observed in CF₃CCl₃. ^bThe contribution from isomer III is only approximate, since the center lines of the spectra are affected by quartz signals.¹⁰ ^cReference 10; observed in CF₂ClCFCl₂.

Since shorter bond lengths normally are associated with larger force constants, the deuterium atoms are expected to preferentially occupy the out-of-plane positions. This is verified by the results in Table II, which reports the calculated zero-point energies for the different rotational isomers of the *n*-butane-1,1,4,4-*d*₄ cation, and Table IV, which gives the same data for the *n*-butane-1,4-*d*₂ cation. As shown in the tables, the rotational isomers with all deuterium atoms in out-of-plane positions (type I) have the lowest energy in both the trans and gauche conformations of both compounds studied. Those rotational isomers which have one deuterium atom in an in-plane position (H5 or H6) and the others in out-of-plane positions (type II) have a ZPE energy which is 0.4–0.6 kJ/mol higher, while the isomers of type III, with two deuterium atoms in in-plane positions (both H5 and H6), have

Table VI. Calculated and Observed Isotropic Proton Hyperfine Coupling Constants in the *n*-Butane Cation (in Gauss)

method	H1, H2	H3, H4	H5, H6	H7, H8	H9, H10	ref
Trans						
SDCI/([5s,3p]/[4s])// HF/3-21G*	0.6		40.0	4.7		6
SDCI/([5s,3p]/[4s])// HF/6-31G**	1.5		38.9	4.7		this work
SDCI/([5s,3p]/[4s])// MP2/6-31G*	2.4		45.8	4.2		this work
SDCI/([5s,4p,1d]/[4s,1p])// MP2/6-31G*	4.1		39.9	3.4		this work
Gauche						
SDCI/([5s,3p]/[4s])// HF/3-21G*	0.7	0.7	39.6	3.7	5.9	6
SDCI/([5s,3p]/[4s])// HF/6-31G**	2.0	0.8	38.9	3.7	6.0	this work
SDCI/([5s,3p]/[4s])// MP2/6-31G*	3.0	3.4	44.2	3.0	6.1	this work
SDCI ^a /([5s,4p,1d]/[4s,1p])// MP2/6-31G*	4.4	4.9	39.0	2.4	5.2	this work
SDCI ^b /([5s,4p,1d]/[4s,1p])// MP2/6-31G*	4.7	5.2	38.5	2.3	5.0	this work
Experiment						
CF ₃ CCl ₃ matrix 115 K			59.1		7.5	9
108 K			59	5.5	10	19
77 K		7.4	59	5	10.4	9
CFCl ₃ matrix, 77 K	(-)-5.5		60		7.8	12

^a51 496 spin-adapted configurations. ^b86 867 spin-adapted configurations.

yet another 0.4–0.6 kJ/mol higher energy.

Also included in Tables II and IV are the statistical weights and the relative populations (excluding statistical weight) at 77 K, of the different isomers, calculated under the assumption that Boltzmann statistics can be applied. In Table III, the Boltzmann populations of all isomers of the *n*-butane-1,1,4,4-*d*₄ cation within the categories I, II, and III have been summed to obtain the final abundance ratios at 77 K. The corresponding information for the *n*-butane-1,4-*d*₂ cation is given in Table V for several temperatures from 4 K to 77 K. For comparison, the observed abundance ratios reported by Lindgren et al.^{9,10} are also included in the tables. Table VI, finally, gives the calculated (SDCI) values of the isotropic proton hyperfine coupling constants, obtained at different levels of approximation, together with experimentally reported values.

Discussion

Like the earlier UHF/3-21G* calculations,⁶ the present MP2/6-31G* calculations predict the trans conformation to be more stable than the gauche one, while the experimental spectra, as mentioned in the introduction, were found to agree better with a gauche ground state. The calculated MP2 energy difference between the two conformations is, however, quite small, 0.3 kcal/mol (see Table I). Previous experience^{4,5} has shown that matrix–solvent interactions may reverse the order of states which are separated by several kilocalories/mole at this computational level, although these examples apply to electronic states with quite differing charge distributions, so the situation is not exactly comparable to the present one. In the absence of a detailed treatment of the matrix effects, however, for which no truly satisfactory method presently is available, it is uncertain whether energetic arguments alone are strong enough to conclusively single out one of the two conformations as the more stable one under the actual experimental conditions. We have therefore chosen to follow the original interpretation by Lindgren et al.^{9,10} and to focus on the gauche conformer in the following discussion. As will be seen below, however, this is not a very crucial point, since the gauche and trans results are very similar.

As shown in Table III, the abundance ratio 2.9 : 4.7 : 2.4, obtained at 77 K from the HF/6-31G** calculations for the gauche form of the *n*-butane-1,1,4,4-*d*₄ cation, agrees well with

the observed ratio⁹ of 3.0 : 4.9 : 2.1. The agreement is, as expected, not quite as good for the 3-21G results (2.1 : 5.5 : 2.4), although the deviation from the purely statistical abundance ratio of 1 : 4 : 4 is clearly reproduced also here. The theoretical results for the gauche conformation agree slightly better with experiment than those for the trans conformation.

In the case of the *n*-butane-1,4-*d*₂ cation, an accurate experimental value for the abundance of isomer III was for technical reasons not possible to obtain,¹⁰ so that only the abundance ratio I:II is available for comparison. This ratio was reported as 6 : 3 in CF₃CCl₃ and 4 : 2 in a CFCl₂CF₂Cl matrix,²⁰ in good agreement with our calculated ratio of 6.5 : 3.2. Also here, the agreement is somewhat better for the gauche than for the trans conformation, although the difference here is less relevant on account of the lower experimental accuracy.

The situation at 4 K is, however, quite different from that at 77 K. Here, the experimentally observed abundance ratio for the *n*-butane-1,4-*d*₂ cation is 7:2 for isomers I:II, while a Boltzmann distribution puts essentially 100% probability into the isomer of lowest ZPE, i.e., isomer I. Instead, the ratio 7 : 2 corresponds to the calculated Boltzmann distribution at a much higher temperature, 40–45 K (cf. Table V). This may indicate that thermal equilibration between the different isomers ceases to occur and that the Boltzmann abundances of this temperature are “frozen” as the temperature is lowered further.

Since the equilibration between isomers I–III occurs by means of an internal rotation of the terminal methyl groups, it is interesting to compare existing estimates of rate constants and activation energies for these rotations. Iwasaki and co-workers^{11,12} have studied these parameters for the *n*-butane cation in several different matrices. They report an activation energy of 2.3–2.4 kcal/mol, depending on the matrix, together with a frequency factor of $1.8\text{--}3.9 \times 10^{11} \text{ s}^{-1}$. Insertion of these numbers into an Arrhenius-type rate equation gives a lifetime of a given rotational isomer of about 1 s at 45 K and about 1 min at 40 K, implying that below the latter temperature all rotational rearrangement can be considered to have stopped. The agreement with the temperature range obtained above is, indeed, very satisfactory.

(20) There is apparently an error in the caption to Figure 3 of ref 10. Since the relative abundance of isomers I and II is in the text said to be 4 : 2 at 77 K, the cation must be *n*-butane-1,4-*d*₂ and not *n*-butane-1,1,4,4-*d*₄.

Higher Approximations. Even though the good agreement between theory and experiment described in the previous paragraphs does not indicate an immediate need for improvements of the theoretical model, its adequacy could be challenged on purely theoretical grounds. It is well known that Hartree-Fock vibrational frequencies often are in error by 10% or more.²¹ One could then question the validity of using such calculations to obtain the ZPE, as is presently done.

The next, qualitatively higher, level of approximation would be to include electron correlation in the calculations. For the present system and with the present basis sets, such calculations would be computationally very demanding, even at the simplest level, i.e., second-order perturbation theory (MP2), and have therefore not been attempted. In the case of the methane cation, however, the results of such calculations are available,⁷ which makes a comparison of the two computational levels possible.

We have therefore calculated the ZPE of the three possible geometrical isomers of the deuterated C_{2v} distorted methane cation, CH₂D₂⁺, at the HF/6-31G** level and compared the results with the MP2 results using the same basis.⁷ The ZPE obtained from the (unscaled) HF calculations are 21.7, 22.1, and 22.4 kcal/mol, respectively, for the different isomers. This can be compared with the MP2 results given in ref 7, which are 21.5, 21.8, and 22.1 kcal/mol, respectively. As can be seen, the differences in the ZPE are only of the order of 1%, i.e., one order of magnitude smaller than for some of the individual frequencies. Although this single example clearly is not enough to enable any definite conclusions to be drawn, it does seem to indicate that reasonably accurate ZPE can be obtained also at the Hartree-Fock level.

Hyperfine Coupling Constants. We have in an earlier paper⁶ reported proton hyperfine coupling constants (hcc) for the *n*-butane cation, obtained from SDCI/[5s,3p]/[4s] calculations at the HF/3-21G* optimized geometry. It is therefore of interest to see to what extent these will change when electron correlation is considered in the geometry determination, since very large effects have been found in some previous cases.^{3,5} The results are given in Table VI. Together with a 10% improvement in the dominant hcc (H5, H6), the most important changes occur in the hcc of the methylene hydrogens, whose values increase from less than 1 G to around 3 G. This can be related to the geometrical changes brought about by correlation, of which a shortening of the central, very elongated carbon-carbon bond by 0.1 Å is the most significant, accompanied by a lengthening of all C-H bonds by about 0.01 Å. Inclusion of polarization functions in the basis set used in the SDCI calculations brings about a further increase of the methylene hcc to 4-5 G, while again worsening somewhat the values of the largest hcc.

The increased values of the hcc of H1-H4 give support to the assignment of a non-zero coupling to the methylene protons, as

suggested in ref 9, which was questioned in our previous paper.⁶ It is still, however, not very easy to understand why only two of the methylene protons should have observable hcc in the gauche isomer, as suggested by Lindgren et al.,^{9,10} since both sets of protons (H1, H2 and H3, H4) are predicted to have approximately the same hcc. In this respect, an interpretation in terms of the trans conformer, as suggested by Iwasaki and co-workers,^{11,12} is more consistent with our hcc calculations. (The negative sign of the hcc of H1-H4, which was suggested by Matsuura et al.¹² on the basis of semiempirical INDO calculations, is, however, contradicted by the present ab initio results.)

It can be noticed that, although clearly reproducing the overall pattern of the hcc, the calculations are still in error by approximately 30% for the largest and 50% for the smaller β -proton couplings. An approximate doubling of the size of the CI, from 51 496 to 86 867 configurations, does not change this situation noticeably (cf. Table VI). The difficulty of obtaining accurate values of β -proton couplings has been recognized in earlier work.^{22,23} A series of calculations on unsaturated hydrocarbon radical cations with four to six carbon atoms, using similar basis sets and number of configurations as in the present work,²⁴ also yielded β -proton hcc which in all cases were only 60-70% of the observed ones. At the moment, we cannot suggest a simple remedy for this problem.

Conclusions

We have in the present paper shown that, at temperatures above 40-45 K, it must be assumed that cations of partially deuterated *n*-butane are found in all the nine possible rotational isomers which are related by rotations of the terminal methyl groups, and that the relative abundances of these isomers follow a Boltzmann distribution determined by the vibrational ZPE of the different isomers. At temperatures lower than this, thermal equilibration does not occur, on account of the relatively high barrier of 2.3-2.4 kcal/mol toward rotation of the methyl groups, with the consequence that the Boltzmann distribution is not attained. The present results will have relevance, e.g., for the interpretation of ESR spectra of other deuterated molecules, recorded at intermediately low temperatures, which may not be interpretable in terms of a unique ground-state conformation.

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Registry No. Butane, radical cation, 34479-72-6; butane-1,1,4,4-d₄, radical cation, 112097-10-6; butane-1,4-d₂, radical cation, 112097-11-7.

(22) Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1984**, *80*, 1006.

(23) Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1985**, *68*, 57.

(24) Lunell, S.; Eriksson, L. A.; Huang, M.-B. *J. Mol. Struct. (THEOCHEM)* **1991**, *230*, 263.

(21) See, e.g.: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.