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1-METHYLCYCLOBUTYL CATION AND CYCLOBUTYL CATION AS CLASSICAL IONS (1)

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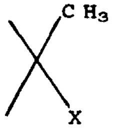
It has been observed that substitution of a methyl group on the site of ionization in secondary aliphatic systems usually produces rate accelerations of 3,000 to 1,000,000 fold (2).

relative rate
1

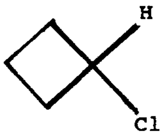


$10^{3.5}$ to 10^{6} faster
X = Cl, TsO, etc.

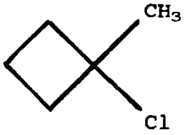
acyclic secondary
systems

(A)

In contrast in the cyclobutyl system (3,4) replacement of the α-hydrogen with methyl produces only a 130 fold increase in the solvolysis rate (5).



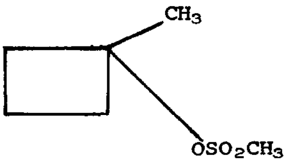
relative rate
1

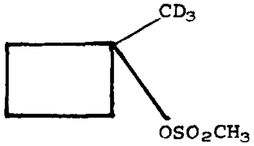


130 fold
faster

(B)

Likewise the α-methyl deuterium isotope effect (4) was found to be only 1.07 ± 0.05 for all three hydrogens.





(C)

$k_H/k_D = 1.07 \pm 0.05$

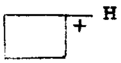
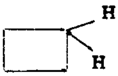
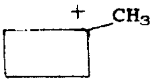
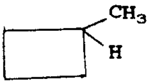
in ethanol at 20°C

The small rate acceleration (130 fold) caused by the methyl group and the very small (7%) isotope effect have both been used to support the conclusion that the cyclobutyl cation (and its 1-methyl derivative) are stabilized by nonclassical resonance into the ring (4,5). Thus both have been used to support the formation of a nonclassical ion.

In the present paper the results are presented on quantum calculations (6) on the cyclobutyl and 1-methylcyclobutyl system. First, calculations were performed on the hydrocarbon and then on its cation with intensive variation (6) of the geometry to locate the minimum in energy (or ground state) in each system. Thus comparisons are made at local energy minima. It is assumed that the transition state will reflect the energy and character of the free ion (see (10)). The results are listed in Table I.

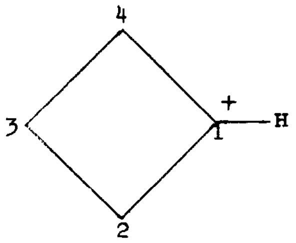
TABLE I

Computed energies in electron volts for various species.

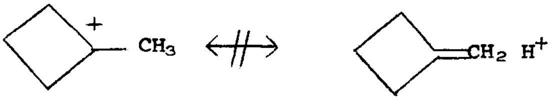
Species (ground state)	Energy ev	Δ E ev
CH_3^+	-110.3356	29.4563
CH_3H	-139.7919	
 Ref. (8)	-388.2864	28.7270
	-417.0134	
$CH_3CH_2^+$	-215.2884	28.3846
CH_3CH_2H	-243.6730	
	-492.5888	28.0766
	-520.6654	

The rate acceleration in acyclic systems is $10^{3.5}$ to 10^{6} in rate or 4.9 to 8.4 kcal/mole in $\Delta G^{\ddagger}$ or about 1/5 to 1/3 of the maximum amount of 24.6 kcal/mole (7-9). If one assumes the same range of the fraction in the cyclobutyl system, the range of rate acceleration due to methyl substitution would be 3.0 to 5.5 kcal/mole or $10^{2.1}$ to $10^{3.9}$ in rate. This range ($10^{2.1}$ to $10^{3.9}$) expected for the cyclobutyl system is to be compared with the $10^{2.11}$ (or 130 fold) acceleration observed in system (B). Thus the cyclobutyl system is completely comparable with the results of a purely classical system; in other words, the small amount of observed rate acceleration is predictable on purely classical grounds.

Of more importance are the computed molecular properties of cyclobutyl ion (8) and 1-methylcyclobutyl ion. Both cyclobutyl ions are most stable when planar in a purely classical form (10). The 1,3 overlap population (11) across the ring is negative [-0.145] indicating nonbonding between carbon atoms 1 and 3 in cyclobutyl ion. Even in a distorted transition state, the overlap population is negative (8).



Of great interest is the amount of positive charge on the methyl hydrogens and the overlap population between C-1 and C-5 (the methyl carbon) in the 1-methylcyclobutyl cation. The C-1 to C-5 overlap is only 0.706 which is less than that in ethyl cation and much less than the value of 1.267 for ethylene. The C-1 to C-3 overlap population is negative (-0.126) and similar to that of the parent cyclobutyl cation. The decrease from -0.126 to -0.145 on removal of the methyl group is in accord with an inductive effect of the methyl rather than important resonance effects. The computed values indicate that the most stable ion I is classical and does not form an important resonance form as in II with an exo double bond to the methyl carbon in the small, strained four-membered ring. Thus the low k_H/k_D value is also explicable on classical grounds.



I II (minor resonance form)

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6. For a discussion of the methods see R. E. Davis and A. Ohno, *Tetrahedron*, **23**, 1015 (1967) and ref. 8.
7. Wiberg using the CNDO/2 method presents data from which we have computed this energy to be 19.2 kcal/mole. See part 2 of ref. 3.
8. R. E. Davis and A. Ohno, *Tetrahedron*, in press. Data are presented on the properties of cyclobutanone, cyclobutyl ion and boretane.
9. For example 1/5 of the bond energy of a sulfur-sulfur bond appears in the activation energy of ionic S_N2 rupture of that bond. See R. E. Davis, J. B. Louis, and A. Cohen, *J. Amer. Chem. Soc.*, **88**, 1 (1966).
10. A nonclassical ion is defined as a structural intermediate (a local minimum in energy) not having a structure predicted by traditional valence theory. A transition state can never be "nonclassical" but an intermediate might be. See Ref. 12 and P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, Inc., 1965, pp. V (last line) and 398 (first line).
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