Electrophilic Cleavage of Cyclopropanes. Acetolysis of Alkylcyclopropanes

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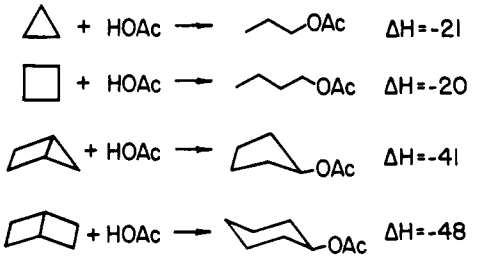
Abstract: The solvent kinetic hydrogen isotope effect showed that proton transfer is at least partially rate determining for the acetolysis of cyclopropanes which span a range of 10^{10} in reactivity. The energies and structures of protonated cyclobutanes were calculated and provide an explanation for the large difference in reactivity between cyclopropanes and cyclobutanes despite their similarity in enthalpies of reaction. The rates and products of acetolysis of a series of alkyl-substituted cyclopropanes were examined. The data, along with the results of ab initio calculations, indicate that for alkyl-substituted cyclopropanes, the protonated species is highly unsymmetrical. Cleavage of the cyclopropane ring always occurs so that the nucleophile becomes attached to the most substituted carbon, but the proton may attack either of the remaining carbons. Proton attack may lead to either retention or inversion of configuration depending on the orientation of the attacking proton with respect to the ring.

The electrophilic cleavage of cyclopropanes has received considerable study.[1-30] The stereochemistry and products of the ring opening of simple cyclopropanes,[2,4,9,12,17,19,24] bicyclic[3,5,8,21,26,31,32] and polycyclic cyclopropanes,[10,11,13,14,20,25,29,30] cyclopropanols,[2,22] and cyclopropyl methyl ethers[2] have been examined. The cleavages of these compounds by mercuric acetate[2,7,15,23] and by halogens[6,9,16,27,28,29] also have been studied. However, relatively few kinetic investigations of the solvolytic cleavage of cyclopropanes have been reported,[19,25,29,32] and questions still remain concerning the structures of the intermediates and the reasons for the variation in stereochemical results. Our interest in the subject has led us to carry out kinetic, tracer, and theoretical investigations of the acetolysis of a variety of cyclopropanes. The results obtained in studying simple alkyl-substituted cyclopropanes are reported herein, and the investigation of bicyclic cyclopropanes will be reported in the following paper.

One might think that the enhanced reactivity of cyclopropanes over cyclopentane and similar hydrocarbons should be related to the strain energy which raises the energy of the C–C bonds and may make them more reactive. In this connection, it is interesting to note the difference in reactivity between cyclopropanes and cyclobutanes. The enthalpies of some possible reactions in the gas phase are given below in kilocalories/mole:[33]



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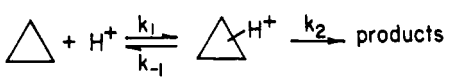
Despite the similarity in enthalpies of reaction of the two pairs of compounds, the reactivities differ greatly. Cyclobutane is essentially inert toward electrophiles whereas cyclopropane has moderate reactivity. Bicyclo[2.1.0]pentane (**1**) is quite reactive, but bicyclo[2.2.0]hexane (**2**) is almost inert. For example, the addition of bromine to a carbon tetrachloride solution of **2** led to an orange solution which persisted for several days.[34] We may first inquire as to the reasons for the unique reactivity of the cyclopropanes.

The reaction of simple cyclopropanes requires acid catalysis in order to achieve a reasonable rate of reaction, and thus the conjugate acid is probably involved. Protonated cyclopropanes are now well-established species, both experimentally[35-46] and theoretically.[47-49] The reaction of a cyclopropane with acetic acid may then be described by



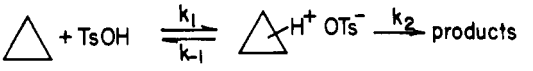
The details of such a process may be examined by using the solvent kinetic isotope effect.[50] In aqueous solution, if k_1 was rate determining, one would expect $k_H > k_D$ via the operation of the normal isotope effect. On the other hand, if k_2 was rate determining, $k_D > k_H$ since D_3O^+ is a stronger than H_3O^+, leading to a higher concentration of the conjugate acid at equilibrium and a larger rate of reaction. The isotope effect for the cleavage of cyclopropane using aqueous sulfuric acid as the solvent was reported by Baird and Aboderin to be k_H/k_D 1.56.[4] This result coupled with the observation that a small amount of deuterium was incorporated into the unreacted cyclopropane during the course of the reaction indicated that in this case, k_{-1} and k_2 had comparable values and both k_1 and k_2 were partially rate determining.

Table I. Vibrational Frequencies

compound	frequencies, cm^{-1}
CH_3OH[a]	3682, 2999, 2844, 1478, 1455, 1334, 1075, 1034, 2970, 1465, 1145, 272 ($\sum$ = 21753)
CH_3OD[a]	3001, 2841, 2718, 1479, 1455, 1225, 1038, 864, 2970, 1463, 1142, 220 ($\sum$ = 20416)
$CH_3OH_2^+$[b]	3516, 3415, 3104, 3088, 2976, 1602, 1437, 1431, 1404, 1180, 1096, 832, 736, 410, 166 ($\sum$ = 26393)
$CH_3OD_2^+$	3104, 3088, 2976, 2576, 2430, 1437, 1431, 1404, 1180, 1146, 1093, 709, 637, 307, 118 ($\sum$ = 23636)
TsOH[c]	2977, 1122, 670 ($\sum$ = 4769)
TsOD[d]	2199, 829, 495 ($\sum$ = 3520)
△	3038, 1479, 1188, 1126, 1070, 3103, 854, 3025 (2), 1438 (2), 1029 (2), 866 (2), 3082 (2), 1188 (2), 793 (2) ($\sum$ = 34700)
	3141, 3120, 3090, 3032, 3029, 3011, 2937, 1501, 1427, 1412, 1391, 1298, 1234, 1207, 1155, 1124, 1017, 966, 850, 844, 700, 436, 66, 47 ($\sum$ = 38035)
	3141, 3120, 3083, 3032, 3028, 2977, 2189, 1500, 1426, 1374, 1278, 1232, 1206, 1187, 1133, 1122, 1013, 922, 849, 725, 670, 433, 64, 43 ($\sum$ = 36747)

[a] Serrallach, A.; Meyer, R.; Gunthard, Hs. H. *J. Mol. Spectrosc.* **1974**, *54*, 94. [b] From ab initio calculation, see text. [c] OH stretching and bending frequencies of CF_3CO_2H in condensed medium: Chackalackal, S. M.; Stafford, F. E. *J. Am. Chem. Soc.* **1966**, *88*, 4815. [d] Estimated using the ratio of unassociated OH and OD stretching frequencies. [e] Shimanouchi, T. "Tables of Vibrational Frequencies"; National Standard Reference Data Series, National Bureau of Standards: Washington DC, 1972.

In the present case, acetic acid was used as the solvent. It has been found that *p*-toluenesulfonic acid is largely undissociated in this medium.[51] Thus, the reaction with cyclopropane may be written as



Here, the proton (or deuteron) in the reactant *p*-toluenesulfonic acid should have a higher stretching frequency than that for the protonated cyclopropane because O–H bonds normally have higher frequencies than C–H bonds[52] and because of the five-coordinate nature of the carbon to which the proton is bonded. If k_2 was rate determining, one might then find a small normal equilibrium isotope effect, whereas if k_1 was rate determining, a relatively large normal kinetic isotope effect could be found. In order to obtain an estimate of the equilibrium isotope effect, the vibrational frequencies of all the species are needed. They are not available for protonated cyclopropane, and therefore they were estimated via an ab initio calculation of the force field. It is known that the calculated vibrational frequencies are not very sensitive to basis set,[53] and therefore the 3-21G basis was used. The calculated C–H stretching frequencies were scaled by the factor 0.91, and the other frequencies were scaled by 0.88,[54] giving the data shown in Table I. The difference in zero-point energy changes for protonation by TsOH and TsOD differs by only 21 cm^{-1} (60 cal/mol), which is well within the uncertainty in the calculation and would lead to only a very small equilibrium isotope effect (less than 1.1). Thus, any values of k_H/k_D significantly larger than unity must be attributed to a kinetic hydrogen isotope effect.

The values determined in this investigation are shown below (cf. Table IV). The data for the solvent isotope effect for bicyclo[2.1.0]pentane and [3.2.1]propellane will be given in the following paper in this issue. Except for cyclopropane, the values

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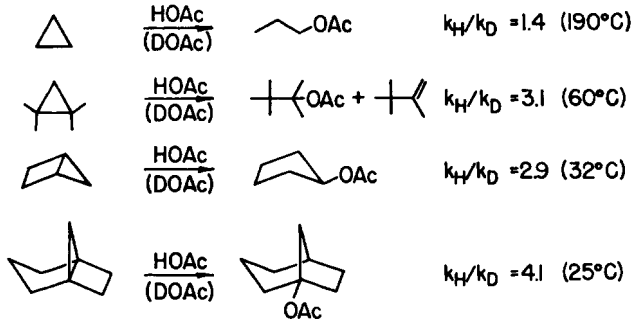
Table II. Calculated Energies

compound	3-21G/3-21G	6-31G*/3-21G	6-31G* RHF	6-31G* MP2	6-31G* MP3
methanol	−114.398 02	−115.033 82	−115.035 42	−115.344 95	−115.360 79
$CH_3OH_2^+$	−114.724 92	−115.336 04	−115.338 99	−115.644 31	−115.662 35
cyclopropane[a]	−116.401 21	−117.058 43	−117.058 87	−117.448 19	−117.476 40
 [a]	−116.705 34	−117.356 94	−117.359 16	−117.737 44	−117.768 77
 [a]	−116.683 23	−117.348 61	−117.350 73	−117.734 15	−117.764 98
cyclobutane	−155.231 32	−156.095 74	−156.097 03	−156.616 57	−156.654 92
	−155.481 43	−156.347 99	−156.350 05	−156.867 14	−156.905 61
	−155.503 53	−156.371 08	−156.372 33	−156.878 51	−156.921 78
propene	−116.424 01		−117.071 46	−117.454 71	−117.484 94
 [a]	−116.726 20		−117.380 76	−117.745 05	−117.780 34
CH_3^+ [a]	−39.009 13		−39.230 64	−39.325 14	−39.341 58
ethylene	−77.600 99		−78.031 72	−78.284 34	−78.305 36

[a] Reference 48d.

are large enough to indicate that k_1 is rate determining. We believe it is also at least partially rate determining with cyclopropane for the following reasons. After 50% reaction, the recovered cyclopropane had only 5% deuterium incorporation. One might suppose that k_2 were rate limiting, but in the step described by k_{-1}, the deuteron initially added was specifically lost in most cases. This would require that rotation of the CH_3^+ group was slow.[55] However, it was also observed that the deuterium in the product *n*-propyl acetate was almost statistically scrambled among all three carbons, indicating that this cannot be the case.[56] Rapid rotation prior to ring opening is required to give this scrambling. Thus, the only conclusion which is consistent with all these observations is that both k_1 and k_2 are partially rate determining.



The above compounds span a range of about 10^{10} in reactivity, but all have proton transfer that is at least partially rate determining. The activated complex probably lies somewhere between the reactant and the corresponding protonated cyclopropane. Since the activation energies are reasonably large, one might expect that the activated complex lies closer to the protonated cyclopropane than to the reactant.

The striking difference in reactivity between cyclopropane and cyclobutane is then probably due to a difference in energy between protonated cyclopropane and protonated cyclobutane. We have given a qualitative explanation for the difference in energy,[32] and Whitten and Pakkanen[49] have presented calculations showing that

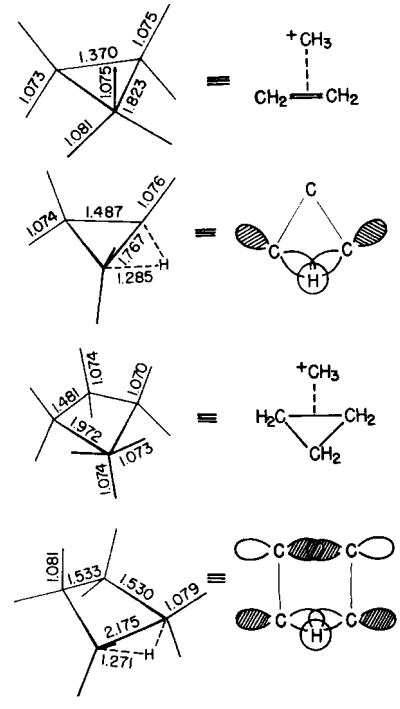


Figure 1. 6-31G optimized geometries for protonated cyclopropane and cyclobutane.

cyclobutane has low basicity. However, at that time it was not practical to carry out a geometry optimization, and the model used may be unrealistic since the cyclobutane ring was assumed not to change its geometry on protonation.

We have obtained the structures of both corner- and edge-protonated cyclobutanes by using the 3-21G and 6-31G* basis sets.[57] Since electron correlation has been found to be important in determining the relative energies of edge- and corner-protonated cyclopropanes,[48d] the MP2 and MP3[58] energies of the protonated cyclobutanes also were calculated by using the 6-31G* geometries. The results are compared with those for cyclopropane[48d] in Table II. The structures are shown in Figure 1.

The equilibrium constants for the protonation of cyclopropane and propene by $CH_3OH_2^+$ have been determined in the gas phase by Franklin and Chong,[39] and from these data, the ΔH_r have been obtained. The ΔE obtained from the calculated energies are given

(55) Theoretical calculations (ref 48c) have shown that rotation of the methyl group should be rapid.

(56) Here, we assume that the path of the attacking deuteron is in the plane of the three-membered ring. Rotation of the CH_2D^+ group is needed in order to place one of the protons in the plane of the ring so that it can be lost, giving cyclopropane-d_1, or migrate to an adjacent carbon, ultimately giving propyl acetate with deuterium at C_1 or C_2. Thus, these two processes are connected. Attack of the deuteron from above the ring to give a CH_2D^+ group rotated 60° from the previous case would have a hydrogen symmetrically placed with respect to the deuteron, loss of H^+ or D^+ would be statistically equally likely, and H^+ loss would be preferred by the kinetic isotope effect. In either case, the small amount of deuterium found in the recovered cyclopropane demonstrates that k_2 cannot be solely rate determining.

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Table III. Protonation Equilibria

B	ΔE, kcal/mol 3-21G	6-31G* RHF	6-31G* MP2	6-31G* MP3	ΔH^a calcd	ΔH obsd
(a) $CH_3OH_2^+ + B \rightleftharpoons CH_3OH + BH^+$						
cyclopropane						
edge	28.1	7.3	8.4	8.1		
corner	14.3	2.1	6.3	5.8	4.8	1.0
cyclobutane						
edge	33.6	18.0	23.5	21.8		
corner	47.5	31.7	30.6	31.9		
propene	15.5	−3.6	5.7	3.9		0.0
(b) $CH_3^+CHCH_3 + B \rightleftharpoons CH_3CH{=}CH_2 + BH^+$						
cyclopropane						
edge	12.7	10.9	2.7	4.3		
corner	−1.2	5.7	0.7	1.9		1.0
cyclobutane						
edge	18.8	21.3	17.8	17.9		
corner	32.6	35.3	25.0	28.0		

[a] Based on MP3/6-31G* energies.

in Table IIIa. They should be corrected for differences in zero-point energies and the change in ΔH on going from 0 to 298 K. This correction may be calculated for the formation of corner protonated cyclopropane using the data in Table I along with the geometries of the compounds and was found to be small (1 kcal/mol).

With both cyclopropane and propene, the correction due to electron correlation is significant, and the MP3/6-31G* values will be used in the following discussion. The calculated ΔE for protonation by $CH_3OH_2^+$ are somewhat larger than the observed values, and this may be due the frozen-core approximation used in the calculations which will not correct for inner-electron correlation on going from a charged to an uncharged atom. It will not be a factor if the proton is transferred from a charged carbon acid to a carbon base. The enthalpy of proton transfer from the isopropyl cation to cyclopropane may be obtained from the experimental data and agrees well with the calculated energy difference (Table IIIb). Thus, the calculated values for the transfer of a proton from the isopropyl cation to cyclobutane also should be satisfactory. Unlike cyclopropane, where the corner- and edge-protonated species have similar energies, there is a large difference in energy between the two protonated cyclobutanes, with the edge-protonated structure having the lower energy. The heat of reaction of cyclobutane with the isopropyl cation is found to be endothermic by 18 kcal/mol, indicating that it should be much more difficult to form the conjugate acid and explaining why cyclobutanes are not readily cleaved by acids.

Why is there such a large difference in the proton affinities of cyclopropane and cyclobutane despite their very similar heats of reactions with acetic acid? The explanation can be found in examining the structures of the conjugate acids (Figure 1). The corner protonated cyclopropane has long bonds from the protonated carbon to the other carbons, and they in turn have a relatively short bond length. Thus, the ion might well be represented by a methyl cation forming a π complex with ethylene. This would be expected to lead to a strong stabilization, and the energy of dissociating the ion to the two species based on experimental data is 74.5 kcal/mol[59] and may be compared with the value of 76 kcal/mol calculated by using MP3/6-31G*. The corner-protonated cyclobutane has even longer bond lengths to the protonated carbon and might be represented as a methyl cation associated with cyclopropane in a fashion similar to an edge-protonated cyclopropane. This association would be expected to be less effective, and the energy of dissociating it to the two species is calculated to be 55 kcal/mol by using MP3/6-31G*.

We may consider the edge-protonated species in a similar fashion. The edge-protonated cyclopropane has a somewhat

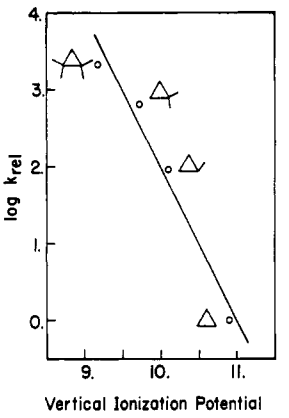
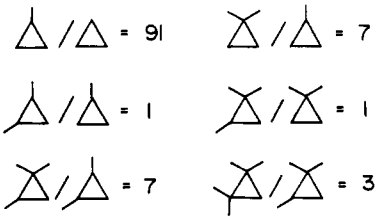


Figure 2. Correlation between log k_{rel} and the ionization potentials for alkylcyclopropanes.

elongated C–C bond at the site of attachment, as would be expected when the two electrons forming the bond are used to form a two-electron three-center bond. This type of bonding would be expected to be facilitated by the bent bonds of cyclopropane, making it possible for the proton to achieve good overlap with the C–C bond orbitals without causing excessive nuclear repulsion with the carbons. It should be much more difficult with cyclobutane since the C–C bonds are only slightly bent. Now, the proton must come much closer to the carbon nuclei in order to achieve good overlap with the C–C bond orbitals. This is seen in the calculated structure which has a much longer C–C bond than the edge-protonated cyclopropane and also is seen in a markedly increased energy. It can be concluded that the unique gometry of cyclopropane makes it possible for relatively facile protonation to occur and that rapid reactions with electrophiles should not be expected for other types of C–C single bonds.

Protonated cyclopropane now appears to be a well-established species with a finite lifetime before rearranging to a more stable ion.[44] The structures of the species formed by protonation of substituted cyclopropanes are not as clear. One way in which the structure of the intermediate in the cleavage of cyclopropanes may be explored experimentally is via an investigation of substituent effects. We have measured the rates of acetolysis of a number of alkyl-substituted cyclopropanes, giving the data summarized in Tables IV and V. The relative reactivities also are given in Table IV. A simple way in which the change in rate might be examined is via a frontier MO approach[60] which would predict that the energy of the activated complex would be related to the energy of the highest occupied MO which has the appropriate symmetry for reaction. The MO would most strongly interact with the empty orbital on the proton. The HOMO energy is linearly related to the ionization potential, and a plot of the logarithms of the relative reactivities against the observed ionization potentials[61] (Figure 2) shows a fair linear relationship. However, the differences in ionization potentials predict that the 1,1-dimethyl/methyl ratio should be smaller than the tetramethyl/dimethyl ratio whereas the opposite is observed. We shall return to this type of relationship when we consider the bicyclic cyclopropane derivatives.

Another way in which to examine the alkyl substitution effects is to consider the rate ratios (Table IV):



(59) Protonated cyclopropane, ΔH_f = 199.8 kcal/mol (ref 39); methyl cation, ΔH_f = 261.8 kcal/mol (Beauchamp, J. L.; Houle, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 4067); ethylene, ΔH_f = 12.5 kcal/mol (ref 33).

(60) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

(61) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 196. Bischof, P.; Heilbronner, E., Prinzbach, H.; Martin, H. D. *Helv. Chim. Acta* **1971**, *54*, 1072.

Table IV. Rates of Acid-Catalyzed Acetolysis of Cyclopropanes[a]

compound	T, °C	k, sec^{-1}	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$
△	190.0	(1.95 ± 0.04) × 10^{-4}		21.6 ± 1.1[e]	−30 ± 2
	180.0	(1.20 ± 0.06) × 10^{-4}			
	170.0	(5.63 ± 0.13) × 10^{-5}			
	160.0	(3.83 ± 0.17) × 10^{-4}			
	(100.0)	5.48 × 10^{-7}	1		
	190.0[b]	(1.39 ± 0.06) × 10^{-4}			
	130.82	(4.27 ± 0.19) × 10^{-4}		19.7 ± 0.6	−26 ± 1
	130.60	(4.19 ± 0.02) × 10^{-4}			
	98.88	(3.45 ± 0.26) × 10^{-5}			
	89.20	(2.73 ± 0.11) × 10^{-5}			
	(100.0)	5.00 × 10^{-5}	91		
	94.99	(2.60 ± 0.04) × 10^{-4}		15.4 ± 0.9	−34 ± 2
	72.60	(6.24 ± 0.33) × 10^{-5}			
	(100.0)	3.50 × 10^{-4}	639		
	120.00	(1.53 × 10^{-4}		15.6 ± 0.6	−37 ± 1
	79.75	(1.41 ± 0.07) × 10^{-5}			
	(100.0)	4.98 × 10^{-5}	91		
	79.75	(1.34 ± 0.01) × 10^{-4}		12.3 ± 0.9	−42 ± 3
	59.75	(4.42 ± 0.24) × 10^{-5}			
	(100.0)	3.66 × 10^{-4}	668		
	59.90	(1.28 ± 0.09) × 10^{-4}		12.9 ± 0.8	−38 ± 2
	39.86	(3.44 ± 0.06) × 10^{-5}			
	(100.0)	1.17 × 10^{-3}	2135		
	59.87[c]	(5.03 ± 0.38) × 10^{-5}			
	187.50[d]	(5.75 ± 0.14) × 10^{-4}		14.2 ± 0.7	−43 ± 2
	145.30[d]	(1.09 ± 0.01) × 10^{-4}			

[a] The reactions were carried out using 0.005 M *p*-toluenesulfonic acid. [b] Rate was measured in acetic-d_1 acid (93% OD). k_H/k_D(corr) = 1.4. [c] Rate was measured in acetic-d_1 acid (90% OD). k_H/k_D(corr) = 3.1. [d] Rate of uncatalyzed reaction. [e] Error in activation parameters are based on a 4% average error in the rate constants.

Table V. Products from the Acetolysis of Cyclopropanes[a]

compounds	products
△	100% OAc
	67% OAc + 22% + 11% (c+t)
	10% OAc + 80% + 10%
	71% OAc + 29% OAc
	49% + 10% OAc + 8% + 19% + 9% OAc + 6% OAc
	67% + 14% OAc + 16% + 3% + 1% OAc

[a] The reaction conditions are given in the Experimental Section. In several cases the ratio of acetates to alkenes varied with time.

It can be seen that the first methyl substitution has a large effect, and another significant increase in rate is found when the second methyl group is attached to the same site. All other alkyl substitution effects are relatively small. This is the behavior one might expect if the protonated cyclopropane was quite unsymmetrical, allowing primary stabilization at only one site.

In order to determine what type of structure protonated methylcyclopropane would prefer, we have carried out geometry optimization for the ions formed by adding a proton to either the methylene or methine carbons and for the edge-protonated species by using both the 3-21G and 6-31G* basis sets. The second-order correction for electron correlation (MP2) was obtained, but it was not practical to obtain the third-order (MP3) correction. However, for the ions, the difference in MP2 energies is essentially the same as found for the isopropyl cation vs. protonated cyclopropanes. Thus, the effect of the third-order correction should be very similar for the two cases, allowing us to estimate the MP3 energy differences. The energies are given in Table VI, and the structures are shown in Figure 3. The energy of the methine-protonated species was calculated to be 8 kcal/mol higher than that of the methylene-protonated ion, and this agrees with the observation that Markovnikov-type cleavage occurs. Unlike cyclopropane, the calculated structure of the methylene-protonated ion is markedly unsymmetrical.

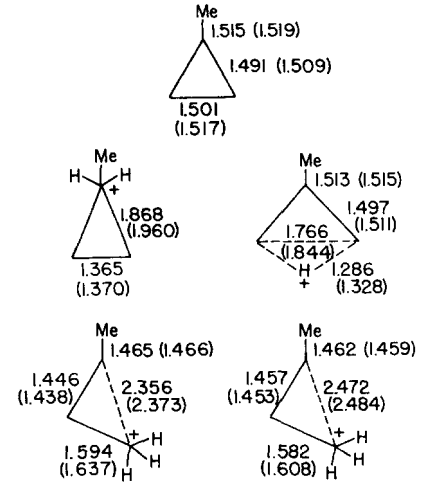
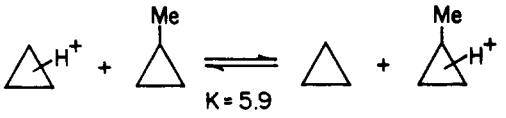


Figure 3. Structures of protonated methylcyclopropanes. The 6-31G* bond lengths are given first, followed by the 3-21G bond lengths in parentheses.

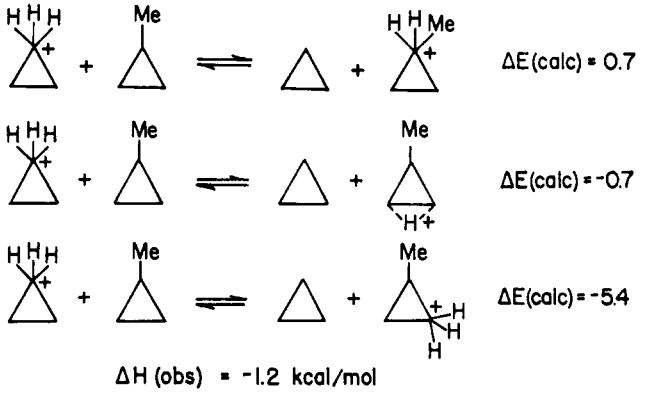
Is it possible that protonated methylcyclopropane is best represented as the 2-butyl cation? We have examined this question by calculating the energy of the best open 2-butyl cation using no symmetry restraints. The structure is shown in Figure 3, and

the energy is given in Table VI. It can be seen that the energy of the 2-butyl cation is only 0.5 kcal/mol lower than that of the methylene-protonated ion. The geometry optimization for the protonated methylcyclopropane was stopped when the gradient became quite small (0.001 hartree/bohr). The similarity in structure and energy between it and the 2-butyl cation indicates that the potential surface is quite flat in this region and that if the geometry optimization had been carried further, the 2-butyl cation would have been reached.

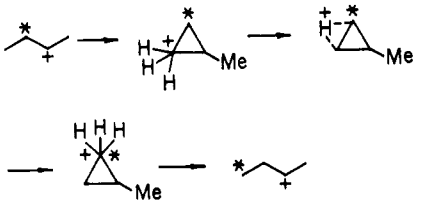
This question of the structure of protonated methylcyclopropane has been examined experimentally by Franklin and Chong[39] who determined the equilibrium constants for the reactions of methylcyclopropane and of *trans*-2-butene with $CH_3OH_2^+$. The $\Delta G°$ for the two reactions were essentially the same, but since the energies of the two hydrocarbons differ by 9 kcal/mol,[33] the two ions which are formed must also differ in energy by this amount. Thus, the protonated methylcyclopropane formed in this experiment is not the 2-butyl cation. From their data, one may also calculate the equilibrium constant for the proton interchange between protonated cyclopropane and methylcyclopropane:



The equilibrium constant is quite small and is not in accord with the kinetically determined relative reactivities or with the difference in calculated structure and energy of the methylene-protonated ion. However, it was interesting to note that the calculated energy change for protonation at the methine carbon (or at the edge) is in excellent accord with the experimental value. The experimental technique used is one which probes the reaction on a very short time scale (10^{-7}–10^{-8} s),[44] and it may be possible that kinetically controlled protonation occurs at the methine carbon.



Protonated methylcyclopropanes are probably involved in the carbon scrambling in the 2-butyl cation observed by Saunders and Hagen.[45] The process may be described by



Our calculations suggest that the corner- and edge-protonated species are not true intermediates but rather are species through which the reaction passes. The activation energy for the scrambling was found to be 7.5 kcal/mol, which is in remarkably good agreement with the calculated energy difference between the 2-butyl cation and edge-protonation methylcyclopropane (7.5 kcal/mol, MP3/6-31G*). It may be noted that the energy differences in the gas phase and in nonnucleophilic ionizing solvents are generally found to be quite similar.[62]

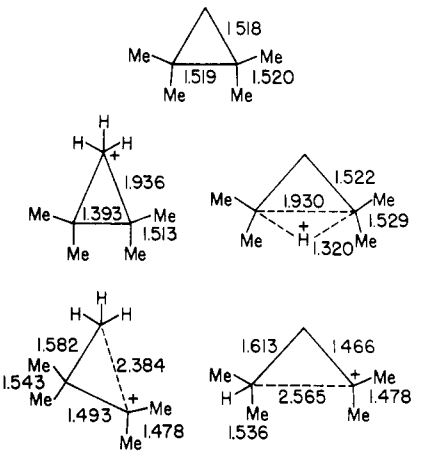
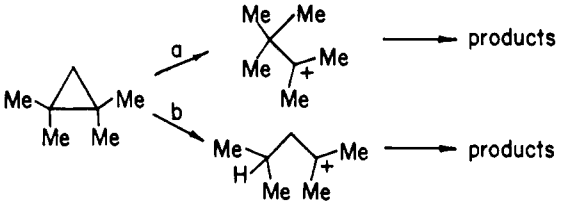


Figure 4. Structures of protonated 1,1,2,2-tetramethylcyclopropane obtained by using the 3-21G basis set.

In the case of 1,2-dimethylcyclopropane,[36] it has been found that HeT^+ reacts in the gas phase to incorporate tritium in the unreacted hydrocarbon. It would be interesting to know where the tritium is located since the conclusions reached concerning methylcyclopropane suggest that it may be at the site of alkyl substitution rather than at the methylene group which would lead to the major products found in solution.

Let us now examine the regiochemistry of the reactions. An examination of the products of acetolysis of cyclopropanes substituted at only one carbon shows that a normal Markovnikov addition occurs (Table V). This corresponds to the formation of the more stable ion. However, when the cyclopropane is substituted at two of its carbons, two types of products are formed. The first is formed via a Markovnikov addition, but the second involves cleavage between the substituted carbons. When 1,1,2,2-tetramethylcyclopropane is used as an example,



Which ions are responsible for the two modes of cleavage? One possible pair is the methylene corner-protonated ion A and the edge-protonated ion B:

Ion A would lead to path a for cleavage, whereas B would lead to path b. On the other hand, the two products could be formed from the unsymmetrical corner-protonated ions C and D which may exist as open cations:

We have carried out geometry optimizations for all four ions using the 3-21G basis set. The energies are given in Table VII,

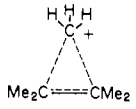
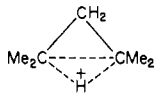
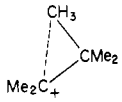
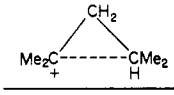
(62) Franklin, J. L. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1968; Vol. I, p 77. Arnett, E. M.; Larsen, J. W., p 457.

Table VI. Energies of Protonated Methylcyclopropanes

compound	3-21G, hartrees	E_{rel}, kcal/mol	6-31G*, hartrees	E_{rel}, kcal/mol	MP2, hartrees	E_{rel}, kcal/mol
methylcyclopropane	−155.223 16		−156.095 81		−156.616 96	
	−155.528 18	14.6	−156.395 66	14.8	−156.905 09	6.1 (8.6)[a]
	−155.510 76	25.5	−156.392 18	17.0	−156.907 32	4.7 (7.5)[a]
	−155.550 77	0.5	−156.418 37	0.5		
2-butyl cation	−155.551 49	0.0	−156.419 24	0.0	−156.914 79	0.0

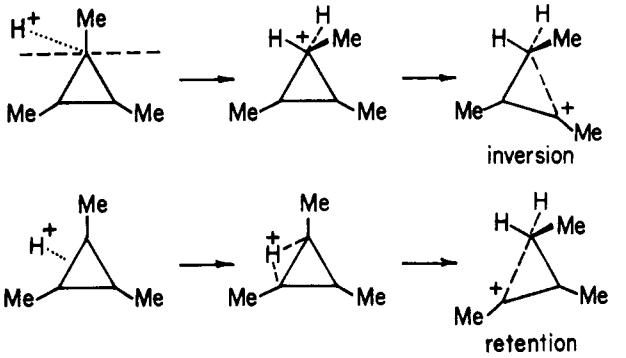
[a] Estimated MP3 relative energies based on a comparison with isopropyl cation and protonated cyclopropanes.

Table VII. Energies of Protonated Tetramethylcyclopropanes (3-21G)

compound	energy	ΔE, kcal/mol
1,1,2,2-trimethylcyclopropane	−271.682 38	
	−272.021 91	10.3
	−272.003 73	21.7
	−272.038 33	0.0
	−272.034 78	2.2

and the structures are shown in Figure 4. The ions A and B have similar energies, but both are much less stable than C and D. The inclusion of polarization functions and electron correlation will probably reduce the energy differences. However, the energy differences are large enough that it seems clear that the cleavage reaction involves the latter ions. Thus, whereas the reaction always proceeds so that the nucleophile becomes associated with the best cationic center, the electrophile does not have a strong preference for which bond it cleaves to form this cation.

We have now considered the nature of the rate-determining step, the reason for the low reactivity of cyclobutanes, the effect of alkyl substitution on the rate of reactions, and the regiochemistry of the reaction. The remaining subject of interest is the stereochemistry of the attack of the proton. DePuy et al.[2i] reported that the *all-cis*-1,2,3-trimethylcyclopropane reacted to give 68% retention of configuration and 32% inversion. Retention corresponds to the cleavage of the C–C bond syn to the entering proton and inversion corresponds to cleavage of the anti C–C bond. We have examined the reason for this stereochemical result by calculating the course of the reaction with a proton. In one calculation, the proton was placed equidistant from two of the ring carbons (1.5 Å) and the structure was allowed to relax by using the gradient technique. Initially, the proton moved closer to the carbons, and the C–C bond distance increased until the structure resembled that of a slightly distorted edge–protonated cyclopropane. Then, the proton began to move toward one of the carbons as the C–C distance continued to increase. This corresponds to attack with retention of configuration. In a second calculation, the proton was placed 2 Å away from one of the ring carbons along a line 30° above the horizontal line through the carbon as shown below. Here, as the proton approached, both C–C bonds increased in length, but the one on the side away from the proton increased more rapidly. This leads to the same final structure as found above, except with inversion of configuration. Thus, proton attack at an edge gives retention and an attack at the backside of one of the C–C bonds gives inversion. The two modes of attack appear to be roughly comparable in energy.



Conclusions. The calculations for protonated cyclopropane and cyclobutane show that the former has unique structural features which makes it much more basic than other cycloalkanes. Whereas protonated cyclopropane is a discrete species, our calculations suggest that substituted protonated cyclopropanes should rearrange to more stable ions with little or no activation energy.

The acetolysis of cyclopropanes normally has proton transfer as the rate-determining step. Open cations are not fully formed before reaction with the nucleophile as indicated by the relatively small rate acceleration due to alkyl substitution[63] and by the generally observed complete inversion of configuration at the site of nucleophilic attack.

Proton attack is relatively unselective between the two positions of attack to give the best carbocation. The direction of proton attack determines whether retention or inversion occurs at the site of attack.

Experimental Section

Materials. Cyclopropane (Matheson), 1,1,2-trimethylcyclopropane, and 1,1,2,2-tetramethylcyclopropane (Wiley Organics) were commercial samples. 1-Methylcyclopropane,[64] 1,1-dimethylcyclopropane,[65] and *cis*- and *trans*-1,2-diethylcyclopropane[66] were prepared by literature procedures. The compounds were analyzed by NMR spectroscopy and, when necessary, were purified by gas chromatography.

Glacial acetic acid was dried by the method of Bruckenstein[67] and was distilled through a Vigreaux column, discarding a generous forerun (bp 116–118 °C). Acetic anhydride was added to give a 2% solution. Acetic-*d* acid was prepared by mixing 102 g (1 mol) of acetic anhydride with 19.6 g (0.98 mol) of deuterium oxide and heating the mixture to reflux for 8 h. It was distilled, collecting the fraction having bp 117 °C.

p-Toluenesulfonic acid monohydrate (Aldrich) was used as obtained. *p*-Toluenesulfonic-*d* acid·D_2O was prepared by mixing 2 g of the monohydrate with 4 mL of deuterium oxide. After 5 min, the solvent was

(63) Alkyl substitution increases the rate of solvolysis by factors of 10^7–10^8: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 226.
(64) Demjanov, N. *Ber.* **1895**, *28*, 22.
(65) Shortridge, R. W.; Craig, R.; Greenlee, K.; Derfer, J.; Booard, C. *J. Am. Chem. Soc.* **1948**, *70*, 946.
(66) Simmons, H.; Smith, R. *J. Am. Chem. Soc.* **1959**, *81*, 4256.
(67) Bruckenstein, S. *Anal. Chem.* **1956**, *28*, 1920.

removed under reduced pressure. The exchange was repeated, and the acid was dried by placing it in a vacuum dessicator.

Kinetics. (a) GC Analysis Solutions of a cyclopropane and an internal standard in acetic acid containing 0.005 M *p*-toluenesulfonic acid were placed in small tubes and sealed. A set of tubes was placed in a thermostat, and after a short time for equilibration, the tubes were withdrawn and cooled at regular intervals. The contents were analyzed by using tandem silver nitrate and OV-101 columns.[68] The ratio of the cyclopropane to the internal standard was determined by using a digital integration. 2-Methylpentane was used as the internal standard for 1,1,2,2-tetramethylcyclopropane, nonane was used with 1,1,2-trimethylcyclopropane, and cycloheptane was used with *trans*-1,2-diethylcyclopropane. The uncatalyzed reactions were studied in the same fashion. In all cases, the data gave good fits to first-order kinetics. In view of the internal return to tosylates observed with bicyclo[2.1.0]pentane (cf. following paper in this issue), we considered whether or not significant concentrations of tosylates could be built up during the reactions of the alkylcyclopropanes. An examination of the rate constants for the solvolysis of the possible tosylates showed that they were sufficiently reactive that if formed, they would not accumulate during the course of the kinetic experiments.[69]

(b) NMR Analysis. Solutions of a cyclopropane were prepared as above and were sealed into NMR tubes. The ratio of compound to internal standard was measured via NMR spectroscopy. A set of tubes was placed in a thermostat and was withdrawn at regular intervals. The ratio was again determined by NMR, giving the amount of cyclopropane which had reacted. Tetramethylsilane was used as the internal standard for cyclopropane, tetrakis(trimethylsilyl)methane[70] was used as the internal standard for methylcyclopropane, and the residual protons in CD_3CO_2D were used as the internal standard for 1,1-dimethylcyclopropane.[68]

(c) Solvent Isotope Effects. The solvent isotope effects were determined in the same way as described above, except that DOAc and TSOD·D_2O were used. The acetic-*d* acid contained 90–93 D, and the rate constants were corrected for the residual H in the DOAc in calculating the isotope effect.

Products.[68] (a) Cyclopropane. Analysis of the products of acetolysis of cyclopropane by NMR showed that only *n*-propyl acetate was formed. When the reaction was carried out in DOAc, the recovered cyclopropane contained ~5% deuterium. Analysis of the *n*-propyl acetate by ^2H NMR showed 27% D at C_1, 23% D at C_2, and 49% D at C_3. The statistical ratio is 28:28:43.

(b) Methylcyclopropane. The NMR spectrum of a tube from the kinetic study which had been heated at 89 °C for 1300 min was determined at 500 MHz and showed the presence of 67% 2-butyl acetate, 11% of a mixture of *cis* and *trans*-2-butene, and 22% 1-butene by comparison with authentic samples.

(c) 1,1-Dimethylcyclopropane. The NMR spectrum of a tube from the kinetic study which had been heated at 90 °C for 104 min was determined at 500 MHz and showed the presence of 10% 2-methyl-2-butyl acetate, 80% 2-methyl-2-butene, and 10% 2-methyl-1-butene by comparison with authentic samples.

(d) *cis*-1,2-Diethylcyclopropane. A solution of the cyclopropane in acetic acid containing TsOH was heated at 120 °C for 102 min. The acetates were isolated by diluting with water and extracting with ether. Analysis by GC using a 10-ft 20% FFAP column at 150 °C indicated 71% 3-heptyl acetate and 29% 4-methyl-3-hexyl acetate as shown by comparison with authentic acetates.

(e) 1,1,2-Trimethylcyclopropane. A portion of the kinetic solution was heated at 60 °C for 23 h. It was diluted with water and extracted into chloroform-*d*. The solution was analyzed by NMR spectroscopy and showed the presence of 49% tetramethylethylene, 10% 2,3-dimethyl-2-butyl acetate, 8% 2,3-dimethyl-1-butene, 19% 2-methyl-2-pentene, 9% 2-methyl-2-pentyl acetate, and 6% 4-methyl-2-pentyl acetate by comparison with authentic samples.

(f) 1,1,2,2-Tetramethylcyclopropane. A portion of the kinetic solution was heated at 60 °C for 4 h. It was diluted with water and extracted into chloroform-*d*. The solution was analyzed by NMR spectroscopy and showed the presence of 63% 2,3,3-trimethyl-1-butene, 13% 2,3,3-trimethyl-2-butyl acetate, 17% 2,4-dimethyl-2-pentene, 7% 2,4-dimethyl-1-pentene, and 2% 2,4-dimethyl-2-pentyl acetate by comparison with authentic samples.

Calculations. Geometry optimizations were carried out by using the program GAMESS[71] until the largest gradient was less than 0.001 hartree/bohr. This generally represented a change in energy of less than 1×10^{-4} hartrees in the last step (0.06 kcal/mol). The MP2/MP3 calculations were carried out by using GAUSSIAN 82.[72]

Acknowledgment. This investigation was supported by NSF Grant CHE-81-21421. The computer was obtained with the aid of grants from the NSF (CHE-8023366) and the Dreyfus and Heyl Foundations. We also acknowledge the support of the NSF Northeast Regional NMR Facility at Yale University.

Registry No. D_2, 7782-39-0; DOAc, 758-12-3; TSOD, 21013-41-2; TSOH, 104-15-4; $CH_3OH_2^+$, 17836-08-7; $CH_3C^+HCH_3$, 19252-53-0; CH_3^+, 14531-53-4; cyclopropane, 75-19-4; methylcyclopropane, 594-11-6; 1,1-dimethylcyclopropane, 1630-94-0; *trans*-1,2-diethylcyclopropane, 71032-66-1; 1,1,2-trimethylcyclopropane, 4127-45-1; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; cyclobutane, 287-23-0; propene, 115-07-1; methanol, 67-56-1; protonated cyclopropane, 17806-70-1; ethylene, 74-85-1.

(68) Further details concerning the experimental procedures may be found in the Ph.D. thesis of S. R. K., 1984.

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