Correlation of Extended Hückel Theory with the Chemical Ionization Reactions of Cyclopropanes

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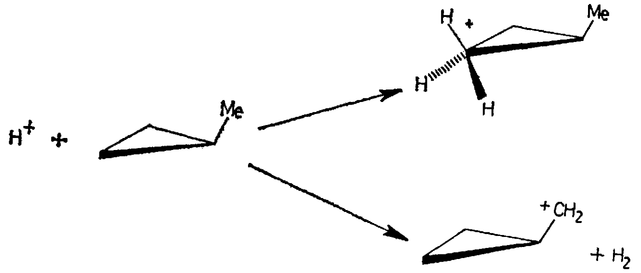
Summary Semi-empirical molecular orbital calculations on the H^+–methylcyclopropane reaction predict two dominant reaction channels: i, proton-addition to the C(1)–C(2) bond leading to a corner-protonated cyclopropane, and ii, hydride-abstraction from methyl giving H_2 and the cyclopropylcarbinyl carbocation; in solution the electrophilic addition pathway predominates, but in the gas phase under chemical ionization conditions both addition and abstraction pathways are not only competitive but their relative rates appear to be highly substituent-dependent.

Extended Hückel molecular orbital (EHMO) calculations on the H^+–methylcyclopropane reaction indicate two energetically favourable paths:[1] i, electrophilic addition of H^+ to the C(1)–C(2) ring bond, and ii, hyperconjugative interaction of H^+ with the methyl H lying over the cyclopropane ring. Hoffmann has suggested[2] that the latter path may involve an intersection with the path defined by hydride-abstraction of methyl H by H^+, alternatively reached by simply taking the hyperconjugative interaction to its extreme.



Further study[3] of the H^+–methylcyclopropane potential energy surface (Figure) by the EHMO method[1] indeed does reveal an exothermic (ΔE_T −94 kcal mol^{-1}) hydride-abstraction pathway leading to the bisected cyclopropylcarbinyl carbocation.[4] Within the proton-addition pathway is found a corner-protonated cyclopropane (E_T −9626 kcal) very similar in structure and bonding properties to the parent C_3H_7 corner-protonated cyclopropane investigated theoretically by Pople,[5] except that the atomic charge on C(1) (+0·41) is larger, because of the directly bonded methyl group, than on C(3) (+0·20), the other four-co-ordinate carbon atom.‡

Figure. Calculated energies along the hydride-abstraction channel.

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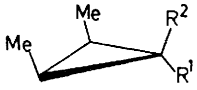
‡ The five-co-ordinate carbon, C(2), has an atomic charge of +0·15 while the corresponding overlap populations are 0·32 for C(1)–C(2) 0·35 for C(2)–C(3), and 0·90 for C(1)–C(3). The entering H^+ remains in the plane of the ring carbon atoms.

This situation is interesting because the reactions of a large variety of cyclopropane substrates in a variety of solvent systems in all cases but one[6] exhibit the proton-addition mechanism,[7] yet the MO calculations predict an equally probable hydride-abstraction process. The rarely observed alkylcyclopropane hydride-abstraction could be highly medium-dependent as are many such ionic reactions. Chemical reactivity without solvation effects can be studied by examining ion–molecule reactions within the ion-cyclotron resonance or mass spectrometer.[8] To test for the relative efficiencies of these two pathways in the gas phase,[9] a methane chemical ionization mass spectrometric study§ has been carried out on a series of phenyl- and methyl-substituted cyclopropanes.¶ The results (Table) are in agreement with the semi-empirical MO calculations. The marked dependence of the addition-abstraction ratios both on the nature of the substituents and on the stereochemical relationship between the substituents reflects the small difference in activation barriers between addition and abstraction pathways in the gas phase.**

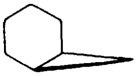
TABLE. Relative ion intensities for proton-addition *vs.* hydride abstraction in the methane chemical ionization of cyclopropanes.

Compound	$(M+\mathrm{H}^+)$[a]	$(M-\mathrm{H}^-)$[a]
(1)	95	5
(2)	76	24
(3)	26	74
(4)	88	12
(5)	88	12
(6)	58	42
(7)	54	46
(8)	51	49
(9)	47	53
(10)	45	55
(11)	43	57
(12)	32	68
(13)	21	79
(14)	15	85

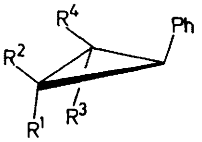
[a] Spectra have not been corrected for natural abundance ^{2}H and ^{13}C. Peak assignments were confirmed with CD_4 chemical ionization.



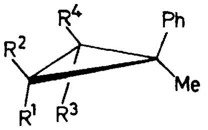
(1) $R^1 = H$ $R^2 = Me$
(2) $R^1 = Me$ $R^2 = H$



(3)



(4) $R^1 = R^2 = R^3 = R^4 = H$
(5) $R^1 = Ph$, $R^2 = R^3 = R^4 = H$
(6) $R^1 = R^2 = Me$, $R^3 = R^4 = H$
(7) $R^1 = R^3 = H$, $R^2 = R^4 = Me$
(8) $R^1 = R^4 = Me$, $R^2 = R^3 = H$
(9) $R^1 = R^3 = Me$, $R^2 = R^4 = H$
(10) $R^1 = R^2 = R^4 = Me$, $R^3 = H$
(11) $R^1 = R^2 = R^3 = Me$, $R^4 = H$



(12) $R^1 = R^3 = H$, $R^2 = R^4 = Me$
(13) $R^1 = R^4 = Me$, $R^2 = R^3 = H$
(14) $R^1 = R^3 = Me$, $R^2 = R^4 = H$

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§ All reactions were carried out on a Finnigan 1015D Mass Spectrometer employing a variable leak inlet, a source temperature of 130 ± 5 °C, a reagent gas inlet pressure of 1·0 ± 0·1 Torr, and an ionization potential of 50 eV.

¶ All cyclopropane reactants were prepared using the methods outlined by DePuy and McGirk. (C. H. DePuy and R. H. McGirk, *J. Amer. Chem. Soc.*, 1974, **96**, 1121). After purification by preparative gas chromatography, each cyclopropane was characterized from spectral data including ^{13}C-n.m.r. spectra.

** The mechanistic conclusions reached here must be qualified to the following extent: the relative ion intensities are those remaining after any fragmentation processes have occurred, which may have an influence on the observed addition-abstraction ratios. With the hope of clarifying this point, ion-cyclotron resonance studies are now in progress to measure the absolute rate constants for abstraction and addition.

[1] A. H. Andrist, *J. Amer. Chem. Soc.*, 1973, **95**, 7531.

[2] Personal communication.

[3] A. H. Andrist, 167th National Meeting of the American Chemical Society, Los Angeles, April, 1974, Abstract PHYS 116. Compare results reported here with the EHT calculations on bicyclobutonium ions: J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, 1968, **90**, 4311; and *ab initio* calculations on the homoallyl and cyclopropylcarbinyl carbocations: W. J. Hehre and P. C. Hiberty, *ibid.*, 1972, **94**, 5917; 1974, **96**, 302.

[4] G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, 1972, **94**, 146; Y. E. Rhodes and V. G. DiFate, *ibid.*, p. 7582; W. C. Danen, *ibid.*, pp. 4835 and 8647; for an earlier summary of the literature, see: J. E. Baldwin and W. D. Foglesong, *ibid.*, 1968, **90**, 4303.

[5] Compare ion (V) in L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 311.

[6] In FSO_3H–SbF_5–SO_2ClF at −100 °C, isopropylcyclopropane undergoes hydride-abstraction giving the dimethylcyclopropylcarbinyl carbocation: G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 1968, **90**, 933.

[7] C. H. DePuy, A. H. Andrist, and P. C. Funfschilling, *J. Amer. Chem. Soc.*, 1974, **96**, 948, and references cited therein.

[8] J. L. Franklin, ed., 'Ion–Molecule Reactions,' Plenum Press, New York, 1972.

[9] Tritium labeling studies implicate protonated cyclopropane intermediates in gas-phase reactions of helium tritiide with *cis*- and *trans*-1,2-dimethylcyclopropane: F. Cacace, A. Guarino, and M. Speranza, *J. Amer. Chem. Soc.*, 1971, **93**, 1088.