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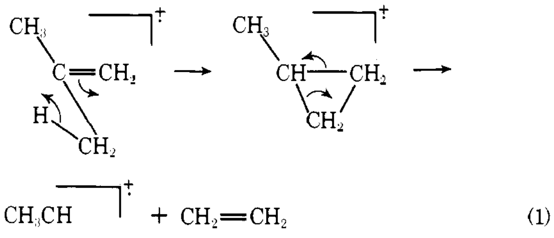
Specific Loss of Ethene from Gaseous 2-Methylpropene Radical Cations in the Picosecond Time Frame. Field Ionization Kinetics

Sir:

Numerous mass spectrometric investigations have emphasized the rich complexity in the gas-phase ion chemistry of $(C_4H_8)^{+\cdot}$ isomers,[2] which when understood will serve as a welcome model for other unsaturated hydrocarbon systems. A pressing requirement to advance the present level of understanding is a mechanism for the facile interconversion of branched and straight-chain structures, and there has been discussion as to the possible involvement of methylcyclopropane intermediates.[2d,h] In this communication, field ionization kinetics (FIK)[3] results are presented for the loss of ethene from 2-methylpropene-*2*-^{13}C and from 2-methylpropene-*1,1*-$[^2H]_2$; these are processes which of necessity involve skeletal rearrangement. These results reveal the intriguing facts that the loss of ethene from 2-methylpropene at short times (picoseconds) following FI is a specific process and that there is an apparent localization of charge during the decomposition. The interpretation proposed here firmly implicates methylcyclopropane-type intermediates in skeletal rearrangements of the $(C_4H_8)^{+\cdot}$ system.

The kinetics of formation of *m/e* 28 and 29 from 2-methylpropene-*2*-^{13}C following FI are shown in the Figure 1a. These two fragments correspond to the fragment *m/e* 28 in the unlabeled compound, attributed to loss of C_2H_4 from the molecular ion.[2c] With 2-methylpropene-*2*-^{13}C, the three fragments *m/e* 40, 41, and 42 are observed corresponding to the two fragments *m/e* 40 (M − CH_4) and 41 (M − CH_3) with the



(1)

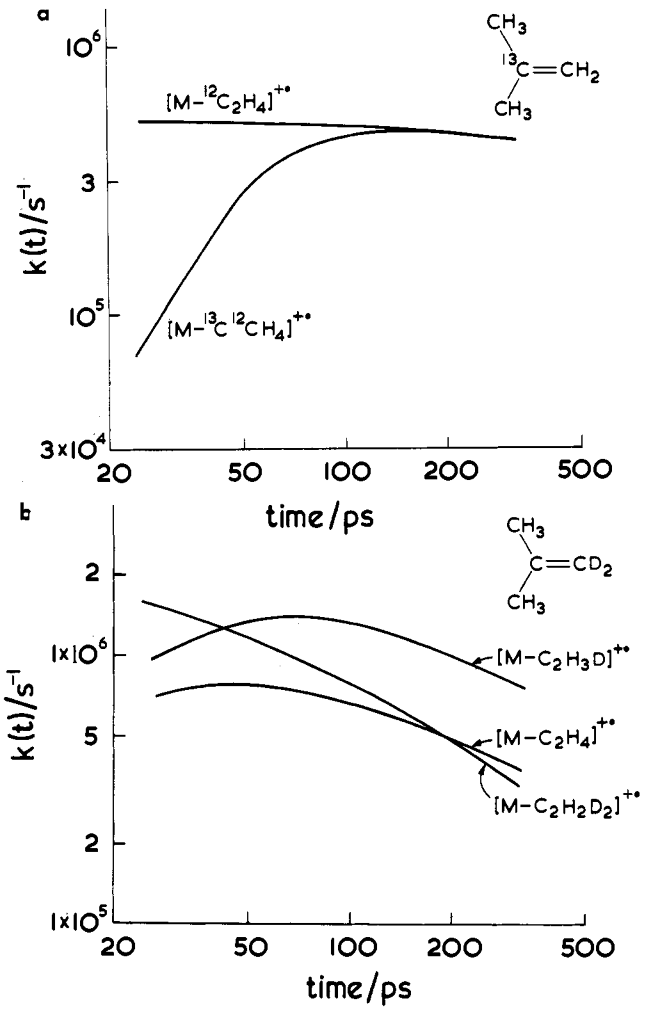


Figure 1. Normalized rates k_t for the loss of ethene from the radical cations produced by field ionization of (a) 2-methylpropene-*2*-^{13}C and (b) 2-methylpropene-*1,1*-$^2H_2$. Normalization is with respect to the measured molecular ion current.[3] To obtain these data, corrections have been made for unlabeled 2-methylpropene impurity, natural isotopic abundance, and fragments formed from $(M + H)^+$ species. Statistical confidence limit in the *ratio* of the rates at any time is ±10%.

unlabeled compounds. Knowing the kinetics of formation of the latter, it is possible to deduce that with the labeled compound there is specific (>95%) formation of *m/e* 42 (M − $^{12}CH_3$) and 41 (M − $^{12}CH_4$) at times <40 ps. On moving to longer times, there is a gradual loss of specificity until at 200-300 ps both processes (loss of methyl and methane) exhibit "carbon randomization". The specific formation at short times of *m/e* 28 (M − $^{13}CCH_4$) from 2-methylpropene-*2*-^{13}C seemingly splits the molecule into halves; yet the charge remains on one half in preference to the other. The sensitivity of the instrument was also sufficient to measure *m/e* 28, 29, and 30 from 2-methylpropene-*1,1*-$[^2H]_2$ (in an earlier FIK study[2i] of this compound only *m/e* 41, 42, and 43 were intense enough to measure), and results are shown in the Figure 1b. Again there is a trend toward specificity (i.e., loss of neutral $C_2H_2D_2$) as time decreases.

The results (Figure 1) are taken as evidence for a specific reaction channel effecting loss of ethene from the 2-methylpropene ion.[4] That the specificity decreases with time is attributed to isomerization prior to decomposition. The lower specificity at 25 ps with 2-methylpropene-*1,1*-$[^2H_2]$ as compared to 2-methylpropene-*2*-^{13}C is explained on the grounds that hydrogen rearrangements (for example, 1,3 allylic hydrogen shifts[2i]) are faster than skeletal rearrangements. The labeling shows that, in the loss of ethene, C-2 forms part of the fragment which retains the charge, whereas the C-1 methylene group is eliminated in the neutral. Thus, if the ionic fragment also had the ethene structure,[5] the labeling evidence would indicate that the charge was being retained by one ethene moiety in preference to the other. Such behavior would hold implication as to relative rates of atomic and electronic reorganizations not easily justified on theoretical grounds. The ionic fragment could, however, correspond to $(CH_3CH)^{+\cdot}$, which has been detected in charge exchange experiments[6] and whose heat of formation has been estimated as being 40 kJ mol^{-1} above that of $(CH_2{=}CH_2)^{+\cdot}$.[7] The results now point directly to a mechanism[8] (eq 1). The charge retention is explained if the activation energy for formation of $(CH_3CH)^{+\cdot}$ and $CH_2{=}CH_2$ is significantly lower than that for formation of CH_3CH and $(CH_2{=}CH_2)^{+\cdot}$. This is true as long as the processes do not have large reverse activation energies, since their heats of reaction are 280 and 580 kJ mol^{-1}, respectively.[9] The second step of the process 1 is supported by FIK measurements on methylcyclopropane.[2k] These show a rapid loss of ethene whose rate steadily increases on moving to shorter times (from ns to 20 ps), i.e., no inflection in the rate/time curve. This behavior is consistent with loss of ethene from the methylcyclopropane radical cation without rearrangement or prior isomerization.

The process depicted in eq 1 provides a link between the branched and straight-chain acyclic $(C_4H_8)^{+\cdot}$ species.[10] Radiolysis experiments have shown that methylcyclopropane ions isomerize to but-2-ene ions and to a lesser extent to 2-methylpropene ions.[2c,f] Similarly FIK measurements suggest that methylcyclopropane and but-2-ene ions isomerize to a common structure or mixture of structures prior to decomposition in 40 ps.[2k] Indeed the conversion of the methylcyclopropane to the but-2-ene ion could be achieved by a process exactly analogous to the first step of the process depicted in eq 1 (i.e., 1,2-hydrogen shift and the swiveling of a C-C bond). Thus, given the conversion of the 2-methylpropene ion to the methylcyclopropane ion as in eq 1, a further similar step can convert the methylcyclopropane to the but-2-ene ion and the link is forged between the linear and branched $(C_4H_8)^{+\cdot}$ isomers.

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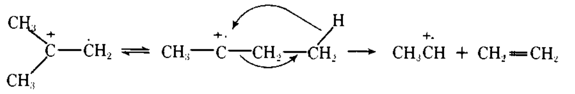

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(10) The transition state bears analogy to the well-documented protonated cyclopropane $(C_3H_7)^+$ system. Molecular orbital calculation (P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 599 (1974)) indicates that the edge protonated cyclopropane ion has an energy 25 kJ mol^{-1} above that of the corner-protonated and 21 kJ mol^{-1} above that of the 1-propyl. Gas-phase experiments suggest that protonated cyclopropane is a stable species with a heat of formation 29–38 kJ mol^{-1} above that of the 2-propyl ion (D. J. McAdoo, F. W. McLafferty, and P. F. Bente, *ibid.*, **94**, 2027 (1972); S.-L. Chong and J. L. Franklin, *ibid.*, **94**, 6347 (1972)). The mechanism to explain hydrogen and carbon scrambling in superacid solution involves edge-protonated cyclopropane ions as transition states between corner-protonated species (M. Saunders, P. Vogel, G. L. Hagan, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973)). See also P. P. Dymerski, R. M. Prinstein, P. F. Bente III, and F. W. McLafferty, *J. Am. Chem. Soc.*, **98**, 6834 (1976).

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Direct Raman Evidence for Resonance Interactions between the Porphyrin Ring System and Ring-Conjugated Substituents in Porphyrins, Porphyrin Dications, and Metalloporphyrins

Sir:

Many porphyrins and metalloporphyrins contain unsaturated substituents which appear from structural formulae to be conjugated with the porphyrin ring system—(1) vinyl and/or acyl groups bound to pyrrole carbons (β substituents) in biological porphyrins and (2) phenyl and other aryl groups bound to bridging methine carbons (meso substituents) in synthetic tetraarylporphines—but the extent and significance of π delocalization linking the porphyrin ring system with unsaturated β and meso substituents is not at all obvious. The pyrrole β-carbon-β-carbon bonds in porphyrins are significantly shorter than other more clearly benzenoid carbon-carbon bonds.[1,2] Although a simple averaging of canonical forms of porphyrin dianions or metalloporphyrins indicates a β-β bond order of 1.75, which can account for the relatively short β-β bonds without ruling out involvement of the β carbons in the delocalized porphyrin π system, the apparent isolated double-bond character[2] of the β-β bond raises doubts about π delocalization that links the porphyrin ring system with unsaturated β substituents. Molecular orbital calculations describing the π systems of porphyrins and metalloporphyrins have been based upon the assumption that the β-β bonds are isolated double bonds; calculations have focussed on the inner 16 atom, 18-π-electron ring that excludes the β carbons.[3] The lack of coplanarity between the porphyrin ring system and *meso*-aryl groups raises doubts about π delocalization that links the porphyrin ring system with *meso*-aryl substituents. Dihedral angles between the porphyrin ring system average plane and *meso*-aryl substituent planes range from ~20° for porphyrin dications through ~60° for neutral, metal-free