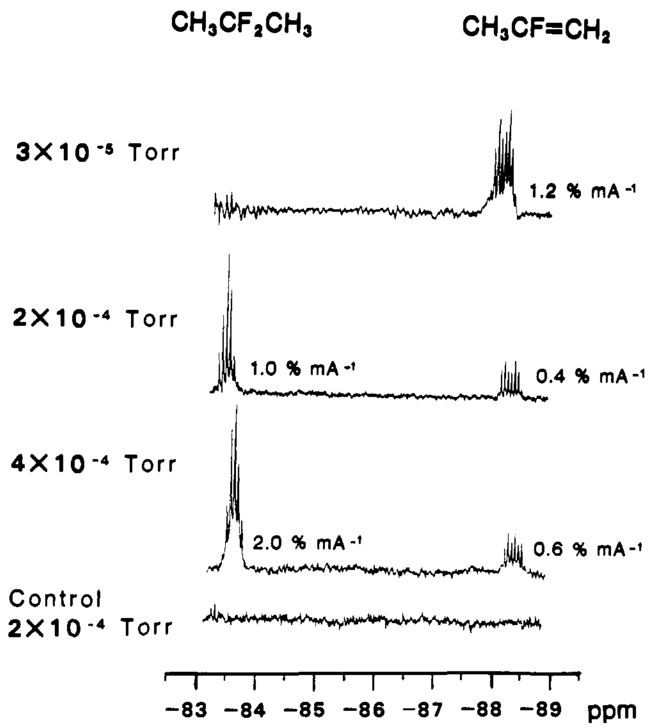


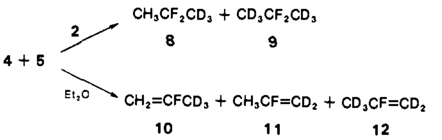
Figure 1. ^{19}F NMR (282-MHz) of neutral products collected from EBFlow radiolysis of *tert*-butyl fluoride at various pressures. Normalized conversions of 2,2-difluoropropane and 2-fluoropropene are expressed as percent of recovered starting material divided by ionizing electron current (% mA^{-1}). Chemical shift relative to $CFCl_3$.

in negligible quantities if the mean free path between reactive collisions is large compared to the dimensions of the reaction vessel. Products that appear only at higher pressures must result from homogeneous gas-phase reactions. Since the mean free path between neutral–neutral collisions is never much shorter than the length of the reaction vessel (even at the highest pressures studied), non-ionic gas-phase reactions can be ruled out.

Neutral products collected in the EBFlow reactor constitute only a small percentage of the recovered starting material. Because of the width of its chemical shift range, its sensitivity, and its dynamic range, ^{19}F NMR was used to examine the recovered material directly, without requiring further purification. As a control experiment, starting material was run through the reaction vessel in a fashion identical with the experimental conditions, but with bias voltages set so that ionizing electrons could not enter the reaction vessel. In this case, ^{19}F NMR showed no substantial products in the recovered starting material.

Figure 1 summarizes our experimental results. EBFlow radiolysis of *tert*-butyl fluoride exhibits a pressure-dependent yield of neutral products. At the lowest pressure, 3×10^{-5} torr, 2-fluoropropene is the predominant product. As pressure is increased, its normalized conversion (percentage relative to unreacted starting material divided by the mean current of ionizing electrons) fluctuates. At the same time, the yield of 2,2-difluoropropane rises markedly and monotonically with pressure. Therefore, ion **3** must be reacting via fluoride abstraction. The production of 2-fluoropropene can be attributed to a combination of non-ionic processes and neutralization of unreacted **3** on surfaces. From the pressure dependence of product yields, we estimate that fluoride abstraction represents >80% of the yield of reaction 2.

EBFlow radiolysis of the deuterated *tert*-butyl fluoride **2** yields neutral products **8** and **9** (reaction 4a) in a ratio of 1.6:1, which is the same as the relative abundances of ions **4** and **5** from 70-eV electron impact on **2**.[13] The ^{19}F NMR resonances of **8** and **9** are



(4a)

(4b)

easily resolved, though it is not possible to determine from ^{19}F NMR whether **8** is mixed with $CD_2HCF_2CH_2D$ (as would arise if ion **4** scrambled its hydrogens internally). But 500-MHz proton NMR[14] of recovered **8** shows no evidence of the scrambled product. A separate experiment provides additional confirmation that hydrogen scrambling does not take place in the 2-fluoroisopropyl cation. Brønsted acid–base reaction with diethyl ether yields **10–12**, as reaction 4b depicts. The three deuterated 2-fluoropropenes from **2** are easily resolved by ^{19}F NMR. Trideuterated compound **10** comes from deprotonation of **4**, and it appears as a doublet of doublets (J = 16 and 48 Hz), which can be assigned on the basis of the spin–spin couplings reported for 2-fluoropropene.[15] If ion **4** had undergone hydrogen scrambling prior to its reaction with base, then two geometrical isomers of $CD_2HCF{=}CHD$ should have been recovered from its deprotonation. There is no indication of any additional products aside from **10–12**.

From the EBFlow experiments we conclude that the 2-fluoroisopropyl cation (a) abstracts fluoride from *tert*-butyl fluoride to yield 2,2-difluoropropane, (b) reacts as a Brønsted acid toward diethyl ether to yield 2-fluoropropene; and (c) does not scramble hydrogens internally on the millisecond time scale during its lifetime in the EBFlow reactor. EBFlow techniques offer new methods for assigning ion structures based on NMR analysis of neutral products from ion–molecule reactions. Quenching gaseous ions by fluoride abstraction represents an especially promising approach.

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[13] Spectrum recorded by Dr. Richard Kondrat on the UCR VG-ZAB high-resolution mass spectrometer. Partial funding for this instrument was provided by National Institutes of Health DRR-BRS Shared Instrumentation Grant RR01750-01.

(14) Spectrum recorded at the Southern California Regional NMR Facility, supported by NSF Grant CHE 79-16324.

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Twist Form of the Ethylene Radical Cation. ESR Studies

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A number of theoretical studies have predicted a nonplanar, twisted structure of the ethylene radical cation, $C_2H_4^{+\cdot}$.[1] However, the twist angle around the carbon–carbon bond calculated is very sensitive to the method used. For example, ab initio SCF-MO-CI[1c] and MNDO[1j] calculations have predicted an ca. 25° twist, whereas calculations by electronic force theory[1f] and MINDO/3[1g] have resulted in an ca. 45° twist. The twist angle of 25° has been confirmed experimentally by vacuum ultraviolet

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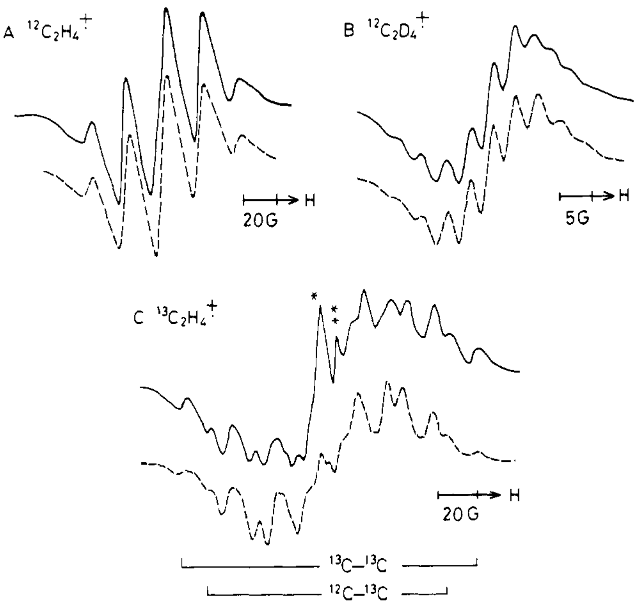


Figure 1. First-derivative ESR spectra of a γ-irradiated solid solution of ca. 0.5 mol % ethylene in Freon-113 recorded at 105 K: (A) $^{12}C_2H_4^{+\cdot}$, (B) $^{12}C_2D_4$, and (C) $^{13}C_2H_4^{+\cdot}$. The simulated spectra are shown as the dotted lines. For the $^{13}C_2H_4^{+\cdot}$, the two spectra of $^{13}CH_2$–$^{13}CH_2^{+\cdot}$ and $^{13}CH_2$–$^{12}CH_2^{+\cdot}$ were superimposed with their respective fractions of 0.81 and 0.18. See the text for further details of the simulation. Signals marked as an asterisk and double asterisks correspond to radicals in the matrix and the damaged spectrosil sample tube, respectively.

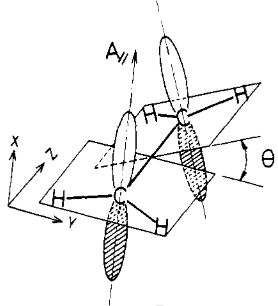
studies of the first Rydberg state of C_2H_4[1d] and analysis of the vibrational structure of the photoelectron spectrum.[1h] ESR spectra of the cation radical, if observed, provide more definite evidence for a twisted structure because of a high sensitivity of hf parameters to the structure. Recent development of radiolytic production of radical cation in Freon and in other halogenated matrices[2] made it possible to observe the twisted trimethylsilyl- and methyl-substituted ethylene radical cations by ESR.[3,4] Here, we want to report conclusive experimental evidence on the twist structure of $C_2H_4^{+\cdot}$, the most simple alkene radical cation, on the basis of the observed ^1H and ^{13}C hf splittings.

Three isotopic species of ethylene cations, $^{12}C_2H_4^{+\cdot}$, $^{12}C_2D_4^{+\cdot}$, and $^{13}C_2H_4^{+\cdot}$, were generated at 77 K by γ-irradiation of solid solutions containing a small amount of parent molecules (ca. 0.5 mol %) in Freon-113 (CCl_2FCClF_2) or Freon-114 (CF_2ClCF_2Cl). ESR spectra observed are shown in Figure 1. The spectrum of $^{12}C_2H_4^{+\cdot}$ (figure 1A) consists of essentially an isotropic quintet of 23.3 G (g_{iso} = 2.0030 ± 0.0003) which is unequivocally attributed to four equivalent protons.

An observation of four equivalent hf splitting of a proton indicates that the spectrum observed is assigned to the ion radical of $^{12}C_2H_4$, not to the neutral radical. Judging from an ionization potential of C_2H_4 (IP = 10.5 eV),[5] the ionic species responsible for the spectrum is, without doubt, the radical cation of $^{12}C_2H_4^{+\cdot}$ which has been generated by a hole transfer from the matrix to the solute. Additional evidence for the integrity of the spectrum was provided by experiments using the isotopic species of $^{12}C_2D_4$ (99 atom %, MSD chemicals). As shown in Figure 1B, the spectrum observed for $^{12}C_2D_4$ was successfully reproduced by reducing the ^1H hf splitting by a factor of 6.5, theoretical ratio of the magnetic moment of ^1H to that of ^2H (D).

On referring to the previously reported α-^1H hf splitting on a π-type planar radical,[6] ca. 10-G ^1H splitting is expected for the planar π-type $C_2H_4^{+\cdot}$ in which an unpaired electron equally occupies 2pπ orbitals of two carbons, whereas the observed isotropic ^1H hf splitting of 23.3 G is about two times larger than that expected for the $C_2H_4^{+\cdot}$ with a planar structure. Consistent with this argument, our INDO calculations result in ^1H splitting of −10.9 G for planar $C_2H_4^{+\cdot}$.[7] Therefore, a planar structure is ruled out for the $C_2H_4^{+\cdot}$.

The observed spectrum of ^{13}C-enriched (90 atom %, MSD chemicals) $C_2H_4^{+\cdot}$ is shown in Figure 1C. As indicated in the figure the hf lines corresponding to ^{13}C–^{13}C (81 %) and ^{13}C–^{12}C (18 %) units are clearly observed at the wing bands, the ^{12}C–^{12}C (1 %) lines being too weak to be detected. ESR spectrum simulations[8] were carried out initially under the assumption that hf splittings of two carbons have axial symmetries whose principal directions were parallel to each other, i.e., an angle (θ) between the directions of parallel hf splittings ($A_\parallel$) of two ^{13}C atoms being zero. The calculated spectra were quite different from the experimental one for any choice of the splittings of $A_\parallel(^{13}C)$ and $A_\perp(^{13}C)$. Next, the calculations were performed with the angle θ as well as the $A_\parallel(^{13}C)$ and $A_\perp(^{13}C)$ as variable parameters. The calculated spectra were much improved, and the best fit spectrum shown in Figure 1C was obtained with $|A_\parallel(^{13}C)|$ = 32.5 and $|A_\perp(^{13}C)|$ = 8.0 G, where the direction cosines of two $A_\parallel(^{13}C)$ were taken as (1, 0, 0) and (0.71, 0.71, 0) with reference to the molecular x, y, z axes, i.e., θ = 45°. As to the ^1H splitting, the observed value of 23.3 G was used directly as the isotropic one.



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As the direction of $A_\parallel(^{13}C)$ is reasonably assumed to be parallel to the 2pπ orbital of the carbon which an unpaired electron occupies, we can conclude that the angle of 45° determined by the present ESR simulation corresponds to the twist angle of $C_2H_4^{+\cdot}$ around the C–C bonding. Judging from the sensitivity of the calculated line shape to the angle θ, it is safe to say that the twist angle of $C_2H_4^{+\cdot}$ in the present system is 45 ± 5°.

Our INDO calculations resulted in a 45° twist at the optimized geometry,[7] similarly to the electronic force theory[1f] and the MINDO/3,[1g] which were consistent with the present conclusion derived from the ESR spectrum analysis. The experimental spin density distribution[9] is compared with the calculated one by INDO as follows: $\rho_{1s}(^1H) = 0.046$ (exptl) vs. 0.076 (calcd), $\rho_{2s}(^{13}C) = 0.005$ (exptl) vs. −0.003 (calcd), and $\rho_{2p\pi}(^{13}C) = 0.42$ (exptl) vs. 0.31 (calcd). The overall agreement is not bad taking into account the assumptions used in the calculations (i.e., neglecting the matrix effect and approximation of INDO).

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