Isotopically Selective CO$_2$ Transverse Excitation Laser Induced Chemical Reactions of Cl$_2$CF$_2$ and Br$_2$CF$_2$ with Olefins

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Abstract: The CO$_2$ transverse excitation laser induced chemical reactions of Cl$_2$CF$_2$ and Br$_2$CF$_2$ with isobutylene, propylene, and ethylene have been investigated. In the (H$_3$C)$_2$C═CH$_2$/Br$_2$CF$_2$ system, evidence for the initial presence of laser-produced difluorocarbene was provided by the isolation of the :CF$_2$-olefin addition compound 1,1-difluoro-2,2-dimethylcyclopropane in the product array. The yield of this product from the (H$_3$C)$_2$C═CH$_2$/Cl$_2$CF$_2$ system was dependent upon the laser irradiation frequency. No analogous *gem*-difluorocyclopropanes were detected in the Br$_2$CF$_2$/H$_3$CCH═CH$_2$ and Br$_2$CF$_2$/C$_2$H$_4$ systems. Carbon isotopic segregation was noted in all experiments. The complex nature of these reaction systems is examined in some detail. The concept of utilizing a laser-produced, isotopically specific reactive intermediate such as :CF$_2$ for the direct synthesis of labeled compounds is presented.

Within the past several years a number of publications have dealt with studies on the laser-induced photodecomposition of various halogenated alkanes.[1-9] A preliminary report from this laboratory described isotopically selective reactions between Cl$_2$CF$_2$ and coreagents such as O$_2$, HCl, NO, and (H$_3$C)$_2$C═CH$_2$ which were promoted by high power density pulses from a CO$_2$ transverse excitation laser.[10] The nature of some of the fluorinated reaction products from these systems was indicative of the initial isotopically selective formation of the reactive intermediate difluorocarbene (:CF$_2$). This conclusion has now been reinforced in further studies where the addition product of :CF$_2$ to (H$_3$C)$_2$C═CH$_2$, 1,1-difluoro-2,2-dimethylcyclopropane (I), has been isolated after laser photolyses in both the Cl$_2$CF$_2$/(H$_3$C)$_2$C═CH$_2$ and Br$_2$CF$_2$/(H$_3$C)$_2$C═CH$_2$ systems.

These systems have now been examined in detail and the studies have been expanded to include the Br$_2$CF$_2$/C$_2$H$_4$ and Br$_2$CF$_2$/C$_3$H$_6$ syrAlems as well.

Experimental Section

Halocarbons were obtained from commercial sources and checked for purity by GLC. Olefins were similarly obtained and subjected to fractionation through traps held at −85 and −196 °C. The material retained at −196 °C was used.

A 972-mL cylindrical stainless steel photolysis cell with a 9.4-cm optical path between NaCl windows was used to contain the reactant halomethane and olefin at 2 and 6 Torr respective nominal partial pressures.

Radiation from NBS-built CO$_2$ TEA laser (0.20-0.27 J/pulse at 2 pps) was focused in the center of the cell with a 25-cm focal length BaF$_2$ lens. A typical laser pulse exhibited a 120-ns width at half maximum and a 700-ns tail. Approximately 82% of the energy of the pulse was delivered within an initial 200-ns interval while the remaining 18% was contained in the peak tail at much lower intensity. Measurements of the essentially rectangular focused laser beam were taken at several distances from the lens by incrementally translating a stainless steel knife edge across the beam (which is coaxial with the y axis) along both the x and z axes. The dimensions of the beam at these various points were then determined from plots of laser power as a function of knife edge position. From these measurements and a knowledge of the cell position in the beam it was estimated that absorber molecules were subject to a maximum power density of the order of 100 MW/cm^2.

After photolysis standard vacuum line techniques were employed to remove the cell contents and included a preliminary fractionation of condensible materials through traps held at −85 and −196 °C. The resultant −196 °C fractions were subjected to GLC at 23 °C on either a 9.1-m 20% squalane on Firebrick or a 6-m 33% fluorocarbon oil on Firebrick column. Individual components were detected by thermal conductivity (TC) and trapped from the carrier stream in efficient borosilicate glass traps for subsequent infrared and mass spectrometric examination.

Component distribution was estimated from electronically integrated GC peak areas assuming equivalent TC detector responses for all materials. Components were identified by comparison of their IR spectra with those of authentic samples and also by mass spectrometry.

The synthesis of 1,1-difluoro-2,2-dimethylcyclopropane was conducted as described by Burton and Naae,[11] the product purified by GLC on fluorocarbon oil, and its identity verified by ^{1}H and ^{19}F NMR and mass spectrometry.

The synthesis of Cl$_2$^{13}CF$_2$ was conducted as given below. A 0.24-mmol sample of commercially obtained ^{13}CCl$_4$ (92.5% ^{13}C by mass spectrometric measurement at m/e 117, 118) was combined with ca. 0.5 g of CaF$_2$ in a 20-mL fused silica bulb. The mixture was maintained at 485-500 °C for 1 h whereupon the volatile materials were removed and treated with dilute, aqueous NaOH for 1 h to remove HCl and SiF$_4$. The resultant volatile materials were separated on a fluorocarbon oil GLC column and the following recoveries achieved: Cl$_2$^{13}CF$_2$ (92.1% ^{13}C by mass spectrometric measurement at m/e 101, 102), 0.071 mmol; Cl$_3$^{13}CF, 0.051 mmol; ^{13}CF$_3$Cl, 0.0036 mmol.

Carbon isotope ratio measurements were made with a commercial 180 °C sector magnetic scanning mass spectrometer. In general, the reported ratios are subject to relative standard deviations of <3%.

Supplementary Experiments. During the investigation of the halomethane/olefin systems it became apparent that some of the products could be formed in secondary processes generally not directly dependent upon the absorption of laser energy. Thus a number of supplementary experiments were carried out in the stainless steel photolysis cell at 23 °C in the dark to assess the probability that these processes might occur during a typical photolysis run. The reactions assessed are summarized in Table I.

In other instances, it was informative to examine the laser photolyses of certain simple systems independently in order to elucidate their possible contributions to the halomethane/olefin systems under study. These photolyses were conducted in the manner described previously and are summarized in Table II.

Results

Typical reaction systems and their principal products along with data concerning the segregation of carbon isotopes are summarized in Table III. In general, the principal products listed for each system comprised 80-90% of the total product array recovered. Each system also produced a number of other components, which could not be unequivocally identified owing to the small quantities recovered. Small amounts (ca. 0.005 mmol) of H$_2$ and CH$_4$ were identified (by mass spectrometry) in systems A and B but measurable amounts of these gases were not found in system C. Systems D and E were not examined for these gases.

Table I. Summary of Supplementary Experiments

Reactants (mmol)	Reaction time, h	Products (mmol)
HCl (0.222) + (H₃C)₂-C=CH₂ (0.333)	4	(H₃C)₃CCl (0.122)
HBr (0.220) + (H₃C)₂-C=CH₂ (0.333)	2	(H₃C)₃CBr (0.154)
Br₂ (0.0446) + C₂F₄ (0.224)	2	(F₂CBr)₂ (0.0339)
HBr (0.110 + H₂C₂ (0.330)	3	No H₂C=CHBr observed

Table II. Summary of Additional Laser Photolysis Experiments

Reactants (mmol)	$\bar{\nu}$, cm⁻¹	Irradn time, h	Products (mmol)
(H₃C)₂C—CH₂ / CF₂ (0.112)	929	2	C₂F₄ (0.0085), (H₃C)₂-C=CH₂ (0.016)
CH₄ (0.33) + Cl₂CF₂ (0.113)	929	4	C₂F₄ + H₂C=CF₂ (0.0432)ᵃ (ClCF₂)₂ (0.0015) HCl (0.112) + other products
(H₃C)₂C=CH₂ (0.334)	929	5	(H₃C)₂C=CH, quantitative recovery with no change
C₂H₄ (0.334) + HBr (0.113)	1082	2	No H₂C=CHBr detected
C₂H₄ (0.334) + Br₂ (0.113)	1082	2	C₂H₄Br₂ (0.0352)

ᵃ These two components could not be separated with the GC columns available.

Since isobutylene was demonstrated to be essentially transparent to the laser frequencies and the conditions used in these experiments, estimates of the average number of photons absorbed per molecule of halomethane consumed could be made for systems A, B, and C from laser power and halomethane consumption measurements. These values are 4600, 8000, and 2100, respectively. The corresponding estimates for systems D and E could not be made since both olefin and halomethane absorbed laser energy.

Discussion

Perhaps the most notable feature of the product array in systems A and C is the presence of 1,1-difluoro-2,2-dimethylcyclopropane (I). The formation of I from isobutylene and :CF₂ generated either chemically, thermally, or by UV irra-

diation has been described by other workers.[11,12] Moreover, in recent experiments in these laboratories, ground state ($^1A_1$) :CF₂ has been identified by its laser-induced ultraviolet fluorescence spectrum in the CO₂ transverse excitation laser photolysis of both Br₂CF₂ and Cl₂CF₂ under collision-free conditions.[13] However, I is not produced in system B which was irradiated at 929 cm⁻¹. The IR spectrum of I indicates significant absorptions in the 930-cm⁻¹ region and CO₂ TEA laser photolyses experiments on I have shown that I is converted into C₂F₄ and isobutylene (cf. Table II). Since I does not significantly absorb IR energy in the 1080-cm⁻¹ region, and therefore is not destroyed, the observed product differences can be explained. No cyclopropanes were recovered from systems D and E. It has been reported that C₂H₄ is not particularly reactive with :CF₂ produced by nonlaser means.[14-16] Moreover, the absorption spectrum of the expected product, 1,1-difluorocyclopropane, shows a strong absorption at 1082 cm⁻¹,[17] suggesting that any cyclopropane formed could be destroyed by subsequent laser pulses. A similar set of possibilities may apply to the propylene system, although no analogous documentation has been found.

The products C₂F₄, HCF₂Cl, and HCF₂Br are characteristic of the dimerization of :CF₂ and the insertion of :CF₂ into the H–X bond of the appropriate hydrogen halide, respectively.[15,18] Alternatively HCF₂Cl and HCF₂Br could also result from a hydrogen abstraction process by a halodifluoromethyl radical as follows: CF₂X· + (H₃C)₂C=CH₂ → CF₂HX + (·C₄H₇).[19] Both HCl and HBr are probably formed by the interaction of halogen atoms released during :CF₂ formation and the olefin present (cf. eq 2). Significant quantities of *tert*-butyl halides are produced in the isobutylene systems. Experimentally it has been found that both HBr and HCl react readily with isobutylene (cf. Table I) in the stainless steel cell, without laser photolysis to form the observed *tert*-butyl halides. Thus the origin of these products is clear. Most probably the 2-bromopropane observed in system D is formed in a similar fashion.
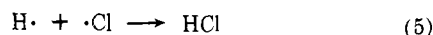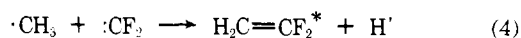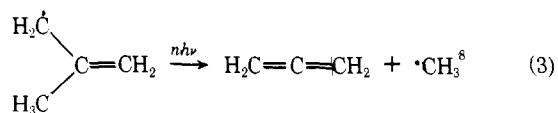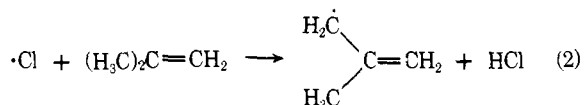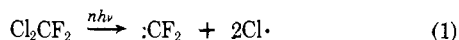
The processes by which H₂C=CF₂ and H₂C=C=CH₂ are formed in systems A and B are not clearly understood. The H₂C=CF₂ shows an altered C isotopic content and possibly results from a :CF₂ reaction with either ·CH₃ or methane. Alternatively, the chlorodifluoromethyl radical may be involved as shown in eq 7, or in a hydrogen abstraction process as mentioned earlier.[19] The 929-cm⁻¹ laser photolysis of Cl₂CF₂ and CH₄ (cf. Table II) gave H₂C=CF₂ as one of the principal products and supports these hypotheses, but does not differentiate between the reactions of :CF₂ and ·ClCF₂.
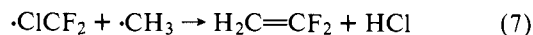
Table III

System	Reactants (mmol taken), β_uᵃ	Laser line (cm⁻¹)	t_{irradn}, h	Principal products (mmol recovered), βᵃ
A	Cl₂CF₂ (0.113) 0.98, (H₃C)₂C=CH₂ (0.334)	R(18) (1077)	4	C₂F₄ + H₂C=CF₂ (0.041)ᵇ 1.3, 1.2, (I) (0.016), (H₃C)₃CCl (0.22) H₂C=C=CH₂ (0.0014)
B	Cl₂CF₂ (0.113) 3.8, (H₃C)₂C=CH₂ (0.334)	P(36) (929)	4	C₂F₄ + H₂C=CF₂ (0.020)ᵇ 0.16, 0.70 HCF₂Cl (0.011) 0.16, (H₃C)₃CCl (0.15), H₂C=C=CH₂ (0.0060)
C	Br₂CF₂ (0.113) 6.4, (H₃C)₂C=CH₂ (0.334)	R(24) (1081)	2	C₂F₄ (0.052) 0.57, (I) (0.0085), HCF₂Br (0.0076) 0.97 (H₃C)₃CBr (0.044)
D	Br₂CF₂ (0.113) 4.6, C₃H₆ (0.334)	R(24) (1081)	2	C₂F₄ (n.d.) 0.71, HCF₂Br (n.d.) 1.1, (H₃C)₂CHBr (0.0330)
E	Br₂CF₂ (0.113) 3.5, C₂H₄ (0.334)	R(26) (1082)	2	C₂H₂ (n.d.), HCF₂Br (0.0047) 1.2, H₂C=CHBr (0.0115), (CF₂Br)₂ (0.0412)

ᵃ The enrichment factor β is defined as R/R_0 where R_0 is the normal ¹³C/¹²C ratio and R is the ratio after photolysis. β_u determined for unconsumed halomethane. R_0 values determined at the respective *m/e* positions for the stated compounds follow: C₂F₄, 100, 101 (0.0106); H₂C₂F₂, 64, 65 (0.0110); Cl₂CF₂, 101, 102 (0.0112); Br₂CF₂, 131, 132 (0.0102); HCF₂Cl, 51, 52 (0.0105); HCF₂Br, 51, 52 (0.0114). ᵇ Compounds not separated with the GC columns used. Combined recovered quantity given and respective β values follow. n.d. = not determined.

The production of allene from isobutylene via the initial formation of an isobutenyl radical ($\cdot C_4H_7$) in shock tube experiments has been described by Tsang.[20] However, samples of isobutylene subjected to the laser photolysis conditions herein described were recovered quantitatively and unchanged from the photolysis cell (cf. Table II). Thus, the allene is not formed directly from a laser-induced decomposition of the isobutylene but rather from some secondary process possibly involving the photofragments of the Cl_2CF_2. Alternatively, one could envision a collisional energy transfer process between vibrationally excited Cl_2CF_2 and isobutylene to give allene. One reasonable sequence of events to explain the formation of both $H_2C_2F_2$ and allene is given in eq 1–6. Alternatively

$$Cl_2CF_2 \xrightarrow{nh\nu} :CF_2 + 2Cl\cdot \quad (1)$$

$$\cdot Cl + (H_3C)_2C{=}CH_2 \longrightarrow \begin{array}{c} H_2\dot{C} \\ \diagdown \\ H_3C \diagup \end{array} C{=}CH_2 + HCl \quad (2)$$

$$\begin{array}{c} H_2\dot{C} \\ \diagdown \\ H_3C \diagup \end{array} C{=}CH_2 \xrightarrow{nh\nu} H_2C{=}C{=}CH_2 + \cdot CH_3{}^8 \quad (3)$$

$$\cdot CH_3 + :CF_2 \longrightarrow H_2C{=}CF_2{}^* + H' \quad (4)$$

$$H\cdot + \cdot Cl \longrightarrow HCl \quad (5)$$

$$H\cdot + \cdot CH_3 \longrightarrow CH_4 \quad (6)$$

steps 4 and 5 may be replaced by the following:

$$\cdot ClCF_2 + \cdot CH_3 \rightarrow H_2C{=}CF_2 + HCl \quad (7)$$

In system E it is interesting to note that no C_2F_4 is found, but rather it is the only system where $(CF_2Br)_2$ is observed. Experiments in the photolysis cell showed that Br_2 and C_2F_4 react readily in the dark at 25 °C to give $(CF_2Br)_2$ (cf. Table I), suggesting that Br_2 is a significant initial product in the photolysis reaction. This type of behavior has been observed previously in laser-photolyses experiments of Cl_2CF_2 with either O_2 or HCl where C_2F_4 was not found.[10] In these cases the $(ClCF_2)_2$ recovered was believed to arise from the demonstrated facile reaction between Cl_2 and C_2F_4. In systems C and D the Br–olefin interaction leads preferentially to HBr formation, thus reducing the probability of Br_2 and consequently $(BrCF_2)_2$ production. On the other hand, Tedder and Walton report that $\cdot CF_2Br$ radicals dimerize to form $(BrCF_2)_2$.[19] In systems A–D, compounds of the type $(XCF_2)_2$ are notably absent. One can alternatively postulate either that $\cdot CF_2X$ species are not produced in significant quantities or that they are generated but are efficiently consumed in other processes such as in methyl hydrogen abstraction reactions with appropriate olefins as mentioned earlier. The evidence presently on hand does not allow an unequivocal distinction to be made between these various alternatives.

The process by which $H_2C{=}CHBr$ is formed in system E is not clearly understood. The data given in Tables I and II indicate that it is not readily produced from HBr and C_2H_2 or from laser-excited C_2H_4 in the presence of either HBr or Br_2.

As noted in Table III, the segregation of carbon isotopes was observed in all systems. This feature is one indication of the direct and rapid utilization of the incident infrared radiation within the vibrational structure of the halomethanes to produce reactive species of predominantly one isotopic form. The use of laser energy to simply heat the system would result in a random distribution of carbon isotopes.

In systems B–E, the ^{12}C species of the halocarbon were irradiated and thus ^{12}C accumulates in the various fluorinated products. When the Cl_2CF_2/isobutylene system (A) is irra-
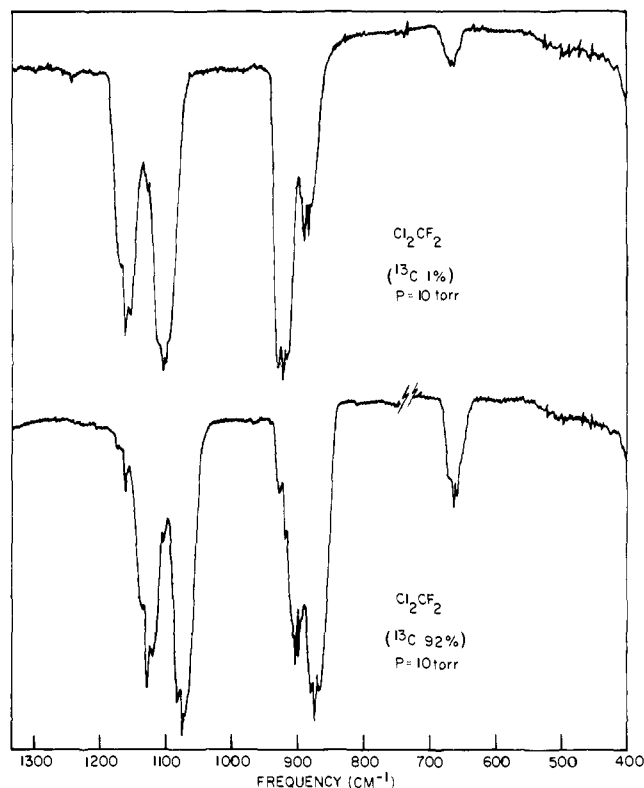

Figure 1. Infrared spectra of Cl_2CF_2 with normal carbon isotopic abundance (top) and enriched in ^{13}C (bottom).

diated at 1077 cm^{-1}, ^{13}C accumulates in the fluorinated products. Similar results were presented in a previous publication for the Cl_2CF_2/O_2 system, irradiated at 1077 cm^{-1}, and likewise support the assignment of this frequency to the $Cl_2{}^{13}CF_2$ species.[10] This assignment has been subsequently confirmed by comparison with the infrared spectrum of authentic $Cl_2{}^{13}CF_2$ prepared in this laboratory. The important features of this spectrum along with that of isotopically normal Cl_2CF_2 are shown in Figure 1. It will be noted in Figure 1 that the $Cl_2{}^{13}CF_2$ species exhibits strong bands centered at 1131, 1077, and 876 cm^{-1}. The bands at 1131 and 1077 cm^{-1} were reported previously from samples of Cl_2CF_2 enriched in ^{13}C through the laser-driven Cl_2CF_2/O_2 reaction.[10] It now becomes apparent that laser-driven selective reactions of this type may have some utility in the assignment of spectroscopic bands for isotopic species or in the convenient preparation of enriched samples for spectroscopic studies.

Unfortunately, an unequivocal assessment of the isotopic composition of laser-produced I could not be made since infrared analysis showed that all samples contained a small amount of an unidentified material (II) of very similar volatility which could not be readily separated with GC columns available. Small samples of II have been isolated from the $Cl_2CF_2/(H_3C)_2C{=}CH$ systems irradiated at 929 cm^{-1} (where I is not found) and mass spectrometric examination suggests that it may interfere with carbon isotope measurements on I. A positive identification of II (if indeed it is a single compound) has been hampered by the small quantities produced in any given photolysis. This problem is undergoing further investigation.

Carbon isotope measurements on the product C_2F_4 indicates ^{12}C enrichment and the unconsumed Br_2CF_2 shows a consistent ^{12}C depletion. However, carbon isotope ratio measurements on samples of product HCF_2Br (at m/e 51, 52) recovered from systems D and E indicate an anomalous accumulation of ^{13}C. At present it is believed that this anomaly arises from interferences by low-level impurities in the samples.

Attempts to verify the HCF_2Br isotopic composition by examining the HCF_2Br^+ ions at m/e 132, 133 have given inconclusive results owing to limited sample size and the sensitivity and resolution limitations of the mass spectrometer.

It is interesting to note that the average photon consumption per molecule of halomethane reacted (2100–8000) is far in excess of the 25–35 photons per molecule required for dissociation on thermochemical grounds. This disparity may be explained through the absorption of photons by many molecules in the focal region with only a few of these achieving sufficient energy to dissociate.

Summary and Conclusions

In the course of these studies it has been possible to prepare macroscopic quantities of fluorocarbon compounds with measurable carbon isotopic enrichments even though the reaction systems in which this is accomplished are quite complex. The reactions may involve both the difluorocarbene diradical and the halodifluoromethyl radical. Other investigators have reported that halodifluoromethyl radicals such as $\cdot BrCF_2$ form straight-chain adducts with olefins rather than cyclopropyl compounds, and tend to dimerize to form $(CF_2Br)_2$ rather than form C_2F_4 through some bromine elimination process.[19,21-24] Thus, in the present study, the fluorinated reaction products C_2F_4 and

$$(H_3C)_2C \overset{\displaystyle CH_2}{\underset{\displaystyle CF_2}{\diagup\!\!\!\!\!\diagdown}}$$
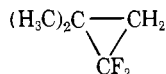
are best explained by the formation of a $:CF_2$ species which then either dimerizes or adds across the unsaturated portion of the olefin. The origin of the products HCF_2Cl, HCF_2Br, and $H_2C{=}CF_2$ is less clearly defined and these could arise from both $:CF_2-$ and $\cdot CF_2X$-hydrocarbon interactions. The general concept of using tuned laser radiation to produce an isotopically specific, reactive intermediate, such as $:CF_2$ or $\cdot CF_2X$, and then utilizing this intermediate in the direct synthesis of labeled compounds appears to be worthy of intensified further investigation.

In addition it has been shown how information obtained from isotopically selective reactions can be utilized in the assignment of infrared absorption bands to specific isotopic species and how the laser-induced chemical approach may offer a convenient method for producing enriched materials for spectroscopic studies.

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Reactivities of Amino and Aminium Radicals: Oxidative Photoaddition of Tetramethyl-2-tetrazene to Olefins

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Abstract: In the presence of oxygen, tetramethyl-2-tetrazene photolytically added to cyclohexene, norbornene, and 1,5-cyclooctadiene under acidic conditions yielding 1-amino-2-hydroperoxides that are reduced to the corresponding amino alcohols. Neither photolysis of the tetrazene under neutral condition nor thermolysis under acidic conditions produced the similar addition compounds. It is concluded that the monoprotonated tetrazene photolytically dissociated to form two dimethylaminium radicals which initiate the attack on carbon–carbon double bonds.

The thermal decomposition of tetraalkyl-2-tetrazenes in dilute acidic conditions, initially reported by Renouf[1] and Fischer and Troschke,[2] has been sporadically reinvestigated mostly using tetramethyl-2-tetrazene (TMT) as a model compound, and has been confirmed to give the alkylidene imines, e.g., $CH_2{=}NCH_3$, as the primary product.[3-6] This thermal reaction is generally interpreted with an ionic pathway

by postulating a dialkylamino diazonium ion[5] or a dialkylnitrenium ion[4] (or its ion pair with a counteranion) as the reactive intermediate.[6-10] On the basis of evidence for the homolytic cleavage of tetraphenyltetrazene in concentrated sulfuric acid, Hammond, Seidel, and Pincock[8] have proposed the aminium radical, the protonated amino radical arising from the bisprotonated tetrazene, as the reactive intermediate. Radical