

Determination of Absolute Product Branching Ratios in Mass Spectrometric Experiments: Detecting Acetyl Radicals at CH_2CO^+

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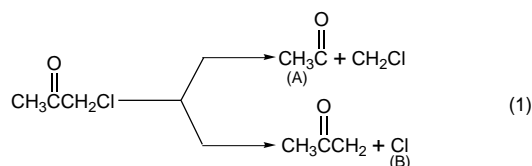
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The paper describes a general method for determining absolute branching ratios in mass spectrometric experiments. The method overcomes the chronic obstacle that the daughter ion fragmentation pattern of radical products is usually unknown. We report the absolute product branching ratio for competing primary C–Cl and C–C bond fission in chloroacetone after excitation on the ${}^1n\pi^*$ absorption band. To determine this branching ratio, acetyl chloride is used to calibrate the relative detection efficiency of acetyl radicals at the CH_2CO^+ daughter ion relative to Cl atoms at ${}^{35}\text{Cl}^+$. We also calculate the daughter ion production probability for CH_2CO^+ formed from internally excited CH_3CO radicals.

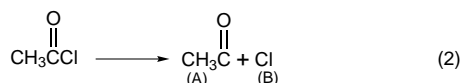
I. Introduction

While mass spectrometric detection and simultaneous determination of the neutral fragment's velocity distribution provide the ability to detect and unambiguously identify almost any molecular or radical product, determining absolute primary product branching ratios can be difficult. Since signal intensity is proportional to the photofragment's ionization cross section, which can be estimated for electron bombardment ionization from atomic polarizabilities,¹ branching ratio determination is easy when only looking at atomic species² that give signal at a single mass to charge ratio. For multiatom product fragments, however, signal is spread among the parent ion of the product and multiple possible daughter ions. This fragmentation in the mass spectrometer is particularly problematic when the product is a vibrationally excited radical, as in many combustion reactions. Traditionally, to determine the absolute branching ratio between competing bond fission channels, one needed an *a priori* knowledge of the daughter ion fragmentation pattern of the radical (something that can change markedly with internal energy³). Another means would be to measure and add signal from the parent and all possible daughter ions, but this practice clearly becomes unwieldy for large molecules or when daughter ions yield signal at masses with high naturally occurring background (e.g. $m/e^+ = 28$, CO^+).

In this paper we present another means of determining absolute branching ratios between primary bond fission channels resulting in the formation of molecular radicals. By determining the observed relative branching for a molecule that has only one primary bond fission channel resulting in the production of fragments A and B in a 1:1 ratio, a relative detection efficiency of A:B can be determined. This relative detection efficiency can then be used to calculate the absolute branching ratio between competing reaction channels where one channel results in the formation of fragment A and the other channel produces B. Specifically, in this paper we determine the absolute branching ratio between primary C–Cl and C–C bond fission in chloroacetone photodissociated at 308 nm, where we only detect the acetyl radical at its CH_2CO^+ daughter ion:



To calibrate detection sensitivity between Cl detected at Cl^+ and CH_3CO fragments detected at the daughter ion CH_2CO^+ , we photodissociate acetyl chloride at 248 nm to generate the C–Cl bond fission products in a 1:1 ratio.



We know of only one prior application of this method of obtaining absolute branching ratios where reactive radicals are involved, in that case to calibrate an atomic versus a diatomic product.⁴ We hope here to introduce this technique to a broader audience by providing a brief general outline of the method and demonstrate its range of utility by applying it to a polyatomic radical, CH_3CO . We also derive the absolute $\text{CH}_2\text{CO}^+/\text{CH}_3\text{CO}$ daughter ion production probability from the data and address the concern about the dependence of the ion fragmentation pattern on the internal energy of the neutral parent radical.

II. Experimental Method

We used a crossed laser–molecular beam apparatus⁵ to measure the photofragment velocities from the photodissociation of acetyl chloride and chloroacetone. After photodissociation with a pulsed excimer laser, neutral dissociation products scatter from the crossing point of the laser and the molecular beam with velocities determined by the vector sum of the molecular beam velocity and the recoil velocity imparted during dissociation. Fragments scattered into the 1.5° acceptance angle of the detector travel 44.13 cm and are ionized by 200 eV electrons. After mass selection with a quadrupole mass filter, the ions are counted with a Daly detector and multichannel scalar with respect to their time-of-flight (TOF) from the interaction region after the dissociating laser pulse. Upon subtraction of the calibrated ion flight time, forward convolution fitting of the TOF

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spectrum determines the distribution of energies released to relative product translation in the dissociation.

The molecular beam was formed by expanding the gaseous sample seeded in He to give a total stagnation pressure of 300 Torr. For the acetyl chloride studies, the sample was freshly distilled to remove any acetic acid contamination, and the bath temperature was fixed at -20°C to give a partial pressure of 29 Torr. Chloroacetone was used as received from Aldrich and expanded at its vapor pressure at 40°C to give approximately a 10% beam in He. The 0.076 mm diameter nozzle was heated to 180°C to prevent cluster formation; the nozzle temperature was calibrated by measuring the peak velocity in a pure He beam TOF. Typical mean beam velocities were 1.41×10^5 cm/s with a full-width-at-half-maximum (fwhm) of 18.2% for chloroacetone and 1.49×10^5 cm/s with a fwhm of 17.8% for acetyl chloride.

To measure the velocity of the parent molecular beam *in situ*, the molecular beam source was rotated to point into the detector and a chopper wheel raised into the beam. To measure the velocities of the neutral photofragments, the molecular beam source is rotated to 10° in the plane containing the beam and detector axis, a plane perpendicular to the laser beam propagation direction. The molecular beam source angle is given here with respect to the detector axis, defined as positive with counterclockwise rotation.

Time-of-flight and measurements were made on acetyl chloride photofragments at 248 nm with the unpolarized output from a Lumonics PM-848 excimer laser and on chloroacetone at 308 nm with a Questek 2860 excimer laser. The light was focused to a 5 mm^2 spot size at the crossing region of the laser and molecular beam, and laser power averaged 185 mJ/pulse for 248 nm and 100 mJ/pulse for 308 nm in this interaction region. Quadrupole resolution was adjusted to 0.9 amu fwhm for $m/e^+ = 35$ (Cl^+) and to 1.0 amu for $m/e^+ = 42$ (CH_2CO^+). Signal was collected at $m/e^+ = 42$ instead of the parent mass $m/e^+ = 43$ (CH_3CO^+) because of better signal to noise ratio. The signal, integrated in many repeated short scans of 20 000 laser shots for each and alternating between each mass, required no additional normalization to laser power.

III. Data and Analysis

Below we have organized the data presentation into three sections. In section A, we determine a relative detection efficiency between $m/e^+ = 35$ (Cl^+) from Cl atoms and $m/e^+ = 42$ (CH_2CO^+) from acetyl radicals using acetyl chloride. In section B we use this calibration to calculate an absolute C-Cl: C-C bond fission branching ratio for chloroacetone. Finally in section C, we further analyze the detection efficiency ratio to extract the daughter ion production probability, $f(42^+/43)$, of the internally excited acetyl radical products of the photofragmentation process.

A. Acetyl Chloride: Detection Efficiency Calibration. We only briefly present dissociation data as it pertains to branching ratio determination; for details on the photodissociation dynamics of acetyl chloride at 248 nm see Person *et al.*⁶ and North *et al.*⁷ Figure 1 shows the photofragment time-of-flight (TOF) spectrum taken at $m/e^+ = 35$ (Cl^+) after 300 000 laser shots resulting from primary C-Cl bond fission after $^1[n(\text{O}), \pi^*(\text{C}=\text{O})]$ excitation at 248 nm. Forward convolution fitting of this spectrum gives the center-of-mass (c.m.) translational energy distribution, $P(E_T)$ shown in Figure 2. This $P(E_T)$ is identical to that reported by North *et al.*⁷ and very similar to that of Person *et al.*⁶

Figure 3 shows the photofragment TOF signal at $m/e^+ = 42$ (CH_2CO^+) after 1 500 000 laser shots. This is the daughter ion

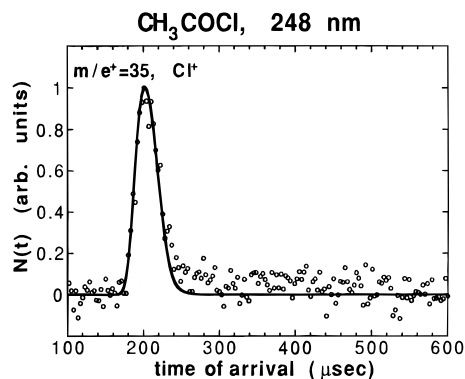


Figure 1. Laboratory time-of-flight spectrum of the photofragments detected at $^{35}\text{Cl}^+$ from acetyl chloride photodissociated at 248 nm. All signal results from primary C-Cl bond fission and is fit with the entire $P(E_T)$ shown in Figure 2.

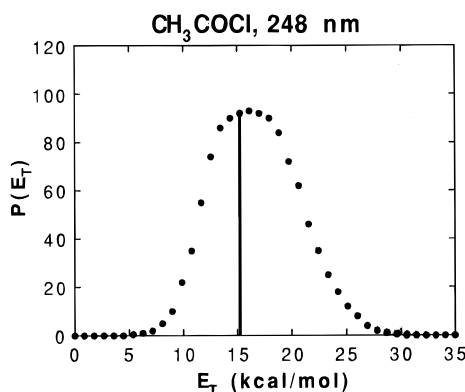


Figure 2. Center-of-mass translational energy distribution, $P(E_T)$, for the C-Cl primary bond fission channel in acetyl chloride at 248 nm. The $P(E_T)$ is derived from the forward convolution fitting of the $^{35}\text{Cl}^+$ spectrum in Figure 1. The solid line at 15.2 kcal/mol indicates where the distribution must be truncated in order to fit the data in Figure 3 due to unimolecular dissociation of the acetyl radical.

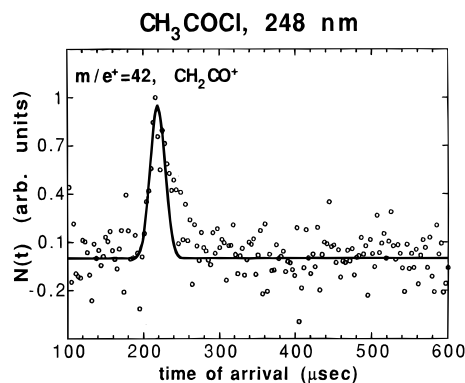


Figure 3. Laboratory time-of-flight spectrum of the photofragments detected at CH_2CO^+ from acetyl chloride photodissociated at 248 nm. All fitted signal results from primary C-Cl bond fission and is fit with the truncated $P(E_T)$ shown in Figure 2. The slow edge which is not fit is likely due to multiphoton processes.

of the acetyl radical fragment which is momentum matched to the Cl atom detected in the $^{35}\text{Cl}^+$ spectrum in Figure 1.⁸ Since acetyl radicals with less than 15 kcal/mol of translational energy have enough internal energy to undergo unimolecular dissociation,⁷ the $P(E_T)$ in Figure 2 is truncated as shown in order to fit the data. The slow edge of this spectrum which is not included in the fit has been found to have a nonlinear dependence on laser power⁹ and is most likely due to the absorption of a photon by acetyl radicals and subsequent C-H bond fission. Since only the early part of the $m/e^+ = 42$ spectrum is used for further

analysis, the presence of this multiphoton signal in no way alters the conclusions herein.

In a photodissociation experiment, observed signal intensities of a given product are obviously not solely a function of the quantum yield for a given photodissociation channel (or branching ratio if two or more product channels compete). Factors such as isotopic abundancies, conversion from c.m. to laboratory scattering reference frames, and the detection efficiency for the photofragments in question also determine the signal intensity. For a detection system composed of a 200 eV electron bombardment ionizer and quadrupole mass filter followed by a Daly detector,¹⁰ detection efficiency ratios are determined by quadrupole throughput, ratios of ionization cross sections and fragmentation to daughter ions in the ionizer. In comparing signal intensity at $m/e^+ = 35$ (Cl^+) from Cl atom photofragments to signal intensity at $m/e^+ = 42$ (CH_2CO^+) from CH_3CO photofragments, these considerations yield the equation

$$\text{obs}\left(\frac{35^+}{42^+}\right) = N\left(\frac{35}{43}\right) f\left(\frac{^{35}\text{Cl}}{\text{Cl}}\right) \text{TS}\left(\frac{35^+}{42^+}\right) \gamma\left(\frac{35^+}{42^+}\right) \quad (3)$$

where obs is observed signal, N is absolute branching ratio, f is isotopic abundance, TS is theoretical signal assuming a 1:1 branching event, (this factor accounts for kinematic corrections and transmission time through the ionizer), and γ is detection efficiency. To determine γ , background subtracted signal was summed over channels 60–69 (corresponding to arrival times of 178.5–205.5 μs) for $m/e^+ = 35$ and channels 67–77 (199.5–229.5 μs) for $m/e^+ = 42$, giving 0.031 78 counts/shot at $^{35}\text{Cl}^+$ and 0.010 56 counts/shot at CH_2CO^+ . Theoretical signal was generated by the program JMSCLB3,¹¹ which corrects for Jacobian factors in the conversion from c.m. to laboratory scattering frames, flux measured in time versus kinetic energy space, and angular and velocity distributions of the scattered photofragments. The relative abundance of the ^{35}Cl isotope, $f(^{35}\text{Cl}/\text{Cl})$, used was 0.7577. Since the only part of the $^{35}\text{Cl}^+$ spectrum used was that which corresponds to acetyl radicals which are energetically forbidden to unimolecularly dissociate, the absolute primary product branching ratio is 1:1 for acetyl chloride photodissociation, as the two fragments result from the same dissociation channel. Rearrangement and substitution into eq 3 yields $\gamma(35^+/42^+) = 5.19 \pm 0.13$.

B. Chloroacetone: Determination of Absolute C–Cl:C–C Branching Ratio. Having calibrated our detection efficiency of $^{35}\text{Cl}^+$ to CH_2CO^+ , we can calculate the absolute branching ratio between C–Cl and C–C primary bond fission channels in chloroacetone ($\text{ClCH}_2\text{COCH}_3$). For a detailed description of chloroacetone photodissociation dynamics at 308 nm in the $^1\text{n}\pi^*$ absorption band see Waschewsky *et al.*¹² Figure 4 shows the photofragment time-of-flight (TOF) spectrum taken after 200 000 laser shots at $m/e^+ = 35$ (Cl^+) (upper frame) and at $m/e^+ = 42$ (CH_2CO^+) (lower frame). All signal can be attributed to primary C–Cl and C–C bond fission and fit with the translational energy distributions shown in Figure 5. Because the C–C bond energy in chloroacetone is approximately 80 kcal/mol and the photon energy at 308 nm is 92.9 kcal/mol, acetyl radicals produced do not have enough internal energy to surmount the 17.2 ± 1.0 kcal/mol energy barrier to unimolecular dissociation; thus, no other corrections are required.

Since the $m/e^+ = 42$ spectrum has overlapping contributions from C–C and C–Cl bond fission, the summed data must be properly scaled to give a number of counts/shot that reflects signal due only to the daughter ion of CH_3CO ; this is not a problem with the $m/e^+ = 35$ data because the early part of the

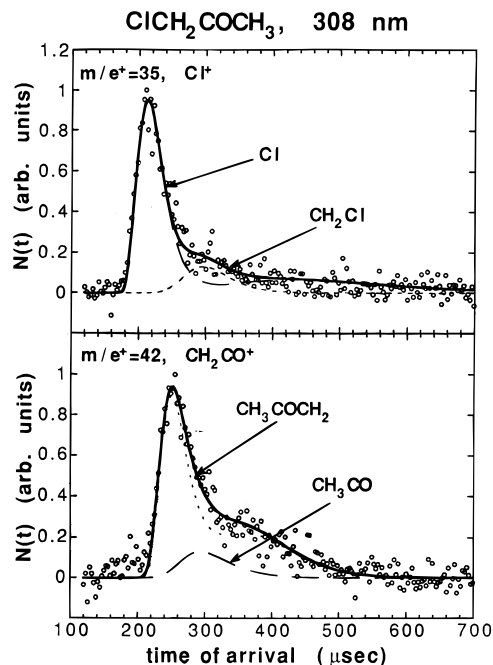


Figure 4. Laboratory time-of-flight spectrum of the photofragments detected at $^{35}\text{Cl}^+$ (upper) and CH_2CO^+ (lower) from chloroacetone photodissociated at 308 nm. All signal results from primary C–Cl or C–C bond fission as indicated and is fit with the $P(E_T)$'s shown in Figure 5. See ref 12 for more detail.

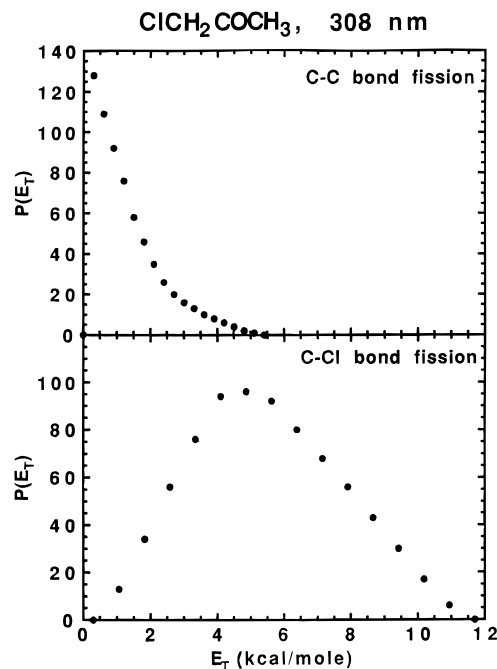


Figure 5. Center-of-mass translational energy distribution, $P(E_T)$, for the C–C (upper) and C–Cl (lower) primary bond fission channels in chloroacetone at 308 nm taken from ref 12. The $P(E_T)$ for C–Cl fission is derived from forward convolution fitting of the portion of the $^{35}\text{Cl}^+$ spectrum which results from primary C–Cl bond fission in the upper frame of Figure 4, while the C–C fission $P(E_T)$ is derived from $^{35}\text{ClCH}_2^+$ data which are not shown.

spectrum results from only C–Cl fission (This is determined by the velocities of the momentum matched CH_2COCH_3 fragments.) Data was processed as above with an integration range of channels 62–78 (184.5–232.5 μs) for $m/e^+ = 35$ and channels 86–115 (256.5–343.5 μs) for $m/e^+ = 42$, giving 0.078 09 counts/shot at $^{35}\text{Cl}^+$ and 0.033 45 counts/shot at CH_2CO^+ . We use an expression similar to eq 3 to determine the C–Cl:C–C primary bond fission absolute branching ratio:

$$N\left(\frac{\text{C-Cl}}{\text{C-C}}\right) = \text{obs}\left(\frac{35^+}{42^+}\right) f^{-1}\left(\frac{35\text{Cl}}{\text{Cl}}\right) \text{TS}\left(\frac{42^+}{35^+}\right) \gamma^{-1}\left(\frac{35^+}{42^+}\right) \quad (4)$$

Using the detection efficiency ratio determined in section III.A and the experimental and theoretical signal intensities for chloroacetone yields $N((\text{C-Cl})/(\text{C-C})) = 4.63 \pm 0.15$ at 180 °C.

C. Determination of Daughter Ion Production Probability. By making two additional assumptions, the detection efficiency, $\gamma(35^+/42^+)$, calculated in section III.A can give a very valuable number, the daughter ion cracking probability of the vibrationally excited acetyl radical upon ionization with 200 eV electrons. Assuming first that ionization cross sections, σ_{ion} , can be estimated from atomic polarizabilities¹ and, second, that the quadrupole throughput is the same for $m/e^+ = 35$ and $m/e^+ = 42$, the daughter ion production probability $f(42^+/43)$ is easily extracted from $\gamma(35^+/42^+)$.

$$\gamma\left(\frac{35^+}{42^+}\right) = \sigma_{\text{ion}}\left(\frac{35}{43}\right) \frac{f(35^+/35)}{f(42^+/43)} \quad (5)$$

Taking ³⁵Cl atoms to be only singly ionized yields $f(42^+/43) = 0.094 \pm 0.002$.

IV. Discussion

This paper presents a method for calibrating absolute branching ratios in mass spectrometric experiments and applies this method by calibrating the relative detection efficiency of Cl atoms and acetyl radicals detected at the CH₂CO⁺ daughter ion in chloroacetone photolysis. The main source of error in the absolute C-Cl:C-C branching ratio results from the relatively low signal to noise (S/N) ratio of the $m/e^+ = 42$ (CH₂CO⁺) acetyl chloride spectrum, giving a 3.1% relative error in the total amount of CH₂CO⁺ signal. Other factors which we have considered but believe to be of minimal importance include (1) ion transmission through the quadrupole, (2) differing initial vibrational states of the acetyl radicals produced from the two molecules, and (3) the possibility of other photodissociation channels in acetyl chloride. The first concern is dismissed by realizing that since we adjusted the resolution to be nearly the same at both masses and the masses detected are similar, we minimized mass-dependent ion transmission, so these factors should result in only a small discrimination against the higher mass.¹³ Note that the fitting programs used fully account for all Jacobian factors and differences in the angular and velocity distributions of the reaction products. The same technique can be applied to the determination of branching ratios in bimolecular reactive scattering experiments.

The question about total vibrational energy of the acetyl fragments can be addressed by simple energy balancing. Acetyl radicals produced from acetyl chloride photodissociation that do not undergo unimolecular dissociation have a mean translational energy of 18.9 kcal/mol, while those from chloroacetone have 1.3 kcal/mol. Subtracting these values and bond energies from the appropriate photon energies results in acetyl fragments produced from acetyl chloride having approximately 13.6 kcal/mol of mean internal energy compared to 11.7 kcal/mol when produced from chloroacetone. This energy difference is unlikely to have much of an effect on the fragmentation pattern of the parent ion in the ionizer. It should be stressed that fragment internal energy is a concern only when internal energy differences are large enough to cause a difference in the ion fragmentation pattern.

Finally, there is some evidence in the literature of a minor C-Cl bond fission channel in acetyl chloride resulting in near-zero translational energy Cl atoms that accounts for $\leq 10\%$ of the total signal.¹⁴ We cannot explain why neither we nor North *et al.*⁷ detect this slow signal, especially since we are more sensitive to slower recoiling fragments in the c.m. frame due to the Jacobian factors. Since the Hess data¹⁴ were taken by photodissociating acetyl chloride at 236 nm, perhaps a new channel is accessed by the increased excitation energy, but this is only speculative. It should also be noted that we do not differentiate between ground (²P_{3/2}) and spin-orbit-excited (²P_{1/2}) Cl atoms because the splitting between these states is only 2.5 kcal/mol, which is below our experimental resolution. All energetic arguments herein and by North *et al.*⁷ have assumed production of only Cl (²P_{3/2}), which is unlikely. Inclusion of a Cl (²P_{1/2}) channel would cause a shift in the truncation point for the acetyl chloride $m/e^+ = 42$ (CH₂CO⁺) $P(E_T)$ and cause some more uncertainty in the determination of $\gamma(35^+/42^+)$. Therefore, we offer 4.63:1.0 as a C-Cl:C-C chloroacetone branching ratio, accounting for the production of both ground and spin-orbit-excited Cl atoms in some undetermined ratio.

Also note that the value of the absolute branching ratio between C-Cl and C-C bond fission in chloroacetone depends markedly on the initial temperature of the expanded chloroacetone. As reported by Waschewsky *et al.*,¹² there is a conformational dependence of the relative rates of C-Cl and C-C bond fission in chloroacetone, with C-Cl fission occurring more readily from the higher energy *trans* conformer.¹⁵ Since heating the nozzle will increase the amount of *trans*-chloroacetone relative to *gauche*-chloroacetone before the supersonic expansion fixes these populations, photodissociation from a hotter sample will result in a larger C-Cl:C-C branching ratio. Thus, the absolute branching ratio determined in this paper of 4.63:1.0 is valid only for a sample at 180 °C, and no quantitative relation can be made between this temperature and those presented in ref 12 since those temperature measurements were calibrated only with a thermocouple and not with He beam time of arrival.¹⁶

The other quantity calculated in this paper, the daughter ion cracking probability of the acetyl radical, also warrants some investigation. Since ion signal was very weak at the parent mass of 43 amu and $<10\%$ showed up at $m/e^+ = 42$, fragmentation must be to lighter masses, most likely $m/e^+ = 28$ (CO⁺). There have been several measurements of the mass spectrum of acetyl radicals produced by a variety of means. Yamashita¹⁷ recorded mass spectra of the photolysis products from simple ketones irradiated in the range 290–320 nm. The spectra obtained at 50 eV for acetyl radicals were dominated by the parent ion, $m/e^+ = 43$, with $m/e^+ = 28$ (CO⁺) and $m/e^+ = 42$ (CH₂CO⁺) each accounting for only about 10% of the total ion signal. This differs from the neutralization-reionization mass spectra recorded by Hop and Holmes,³ which evidence negligible parent ion signal compared to that at the $m/e^+ = 28$ and 42 daughter ions. These workers also observed that the $m/e^+ 28:42$ signal ratio increased with increasing target ionization energy, which offers an explanation as to why we see little signal at $m/e^+ = 43$ and only a small fraction of the total ion signal at $m/e^+ = 42$ (high background signal at $m/e^+ = 28$ makes data collection quite difficult).

We should point out that the calibration method outlined above can also be used on other systems of interest, as the difference in internal energy of the calibrating radicals and radicals used in the branching ratio determination is not so large as to alter the daughter ion fragmentation patterns. Some of

the other systems we have considered include C—Br:C—C fission in bromoacetone, calibrating with acetyl bromide, C—S:S—H fission in methyl mercaptan (CH₃SH) using CH₃SSH, and branching between C—Cl bond fission and molecular HCl elimination in allyl chloride using HCl to calibrate HCl⁺ to Cl⁺ signal intensities. The method is equally applicable to bimolecular reactions with competing product channels.

V. Summary

We have determined for chloroacetone that the absolute C—Cl to C—C branching ratio is 4.63 ± 0.15 at a conformer temperature of 180 °C by the use of a secondary ion signal calibration technique. The technique calibrates the detection efficiency of the acetyl radical product at the CH₂CO⁺ daughter ion relative to the Cl atom product using acetyl chloride photodissociation. This method of calibrating relative ion signal intensities is widely applicable, offering a way to determine competing product channel branching ratios for reactions which produce radical products with unknown ionization cross sections and daughter ion fragmentation patterns.

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References and Notes

(1) Ionization cross sections are estimated by using the empirical relationship $\sigma_{\text{ion}} = 36(\alpha^{1/2}) - 18$ from the following: Center, R. E.; Mandl, A. *J. Chem. Phys.* **1972**, *57*, 4104. The atomic polarizabilities (α) used are 0.666 793 (H), 1.76 (C), 0.802 (O), and 2.18 (Cl) from the following: Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1977**, *13*, 1.

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(8) Since acetyl fragments can recoil from either ³⁵Cl or ³⁷Cl, the effective mass used for the momentum matched partner in our fitting was actually 35.45 amu.

(9) North, S. W. Private communication.

(10) The Daly detector has near quantum efficiency over a wide range of ion masses; see ref 5.

(11) Our forward convolution programs for the c.m. to laboratory frame transformations were adapted from the CMLAB programs written by the Y. T. Lee group.

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(15) The chloroacetone conformer which we refer to here as "trans" should, in correct nomenclature, be called *s-cis*, as the dihedral angle between the C—Cl and the C=O bonds is zero and the Cl and O atoms, having the highest atomic numbers, should determine the groups to which the geometry refers. We retain the nonstandard name *trans*, however, to remain consistent with several earlier studies.

(16) The nozzle temperature is measured during experiments by a chromel—alumel thermocouple which is held near the nozzle tip with only tension. This results in temperature readings which vary with thermocouple position and degree of contact.

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