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Estimation of Atmospheric Lifetimes of Hydrofluorocarbons, Hydrofluoroethers, and Olefins by Chlorine Photolysis Using Gas-Phase NMR Spectroscopy

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An empirical correlation has been derived between accepted atmospheric lifetimes of a set of hydrofluorocarbons and hydrofluoroethers and relative rates of reaction with photolyzed chlorine in excess at ambient temperature. These kinetic systems were studied by nuclear magnetic resonance (NMR) spectroscopy in the gas phase, marking the first application of NMR spectroscopy to this field. The square of the Pearson coefficient *R* for the linear correlation between observed reaction rates and accepted atmospheric lifetimes was 0.87 for compounds of lifetime less than 20 years. The method was extended to the study of ethene and propene; the rate of reaction of propene was found to be 1.25 times that of ethene at 23 °C. The chief advantage of this method is its simplicity and reliance only on common tools and techniques of an industrial chemical laboratory.

A widespread and increasing concern about the role of anthropogenic atmospheric compounds in global climate change has resulted in a renewed intensity of study of the volatile products and byproducts of industrial chemistry. Of special interest are compounds intended for refrigerant and related applications, such as hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs). While newer commercial products do not have the deleterious ozone-depleting effects of the earlier-generation chlorofluorocarbons, some highly stable fluorinated compounds resist facile photochemical degradation in the troposphere and persist in the atmosphere as greenhouse gases. For this reason, it is of great importance to estimate the atmospheric lifetimes of such fluorinated compounds.

As the primary means of tropospheric degradation of many atmospheric pollutants is free-radical attack by hydroxyl radical, laboratory measurements of the rate of reaction of a given compound with hydroxyl radicals can permit a good estimate of likely atmospheric lifetime. Reaction with chloro radicals is another, albeit minor, pathway of atmospheric degradation, proceeding by similar radical mechanisms. Various analytical

methods are practiced for the determination of these reaction rates.¹ These can be classified as direct methods, which measure the concentration of gaseous free radical over time, and indirect methods, which evaluate the products of reaction at intervals. Direct methods have been reported that employ laser-induced fluorescence,^{2,3} simple resonance fluorescence in conjunction with flash photolysis⁴ or fast flow discharge,⁵ and free-radical titration methods.⁶ In the indirect methods, reactions have been studied in situ by long-path IR spectroscopy.^{7,8} Ex situ indirect methods have been reported in which the reaction is carried out in a vessel external to the detection system, and the product species are analyzed, most commonly by Fourier transform infrared spectroscopic⁹ or gas chromatographic^{9–12} techniques.

With heightened attention and regulatory pressure attending the introduction of new volatile commercial compounds, it is of great interest in the chemical industry to obtain knowledge of the environmental fate and atmospheric lifetime of a potential commercial compound as early as possible in the cycle of synthesis, production, and commercialization. While the techniques listed above are valid means of obtaining an estimate of atmospheric lifetime, they generally share the drawback of requiring specialized analytical equipment or reaction apparatus. It was of interest to develop an analytical method to estimate atmospheric lifetimes of new compounds that required only the

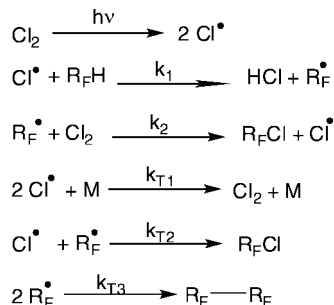
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Scheme 1. Mechanism of Reaction of Chloro Radicals with HFCs



equipment and analytical techniques common to an industrial synthetic chemistry laboratory. The validation of this new method would be achieved by fulfilling two criteria: demonstrating an acceptably accurate empirical correlation between observed reaction rates derived from it and accepted atmospheric lifetimes of known species, and yielding such results on a rapid experimental time scale.

This study examines a fast analytical method that combines chlorine photolysis with NMR spectroscopy in the gas phase. It has previously been applied in our laboratories to kinetic studies of fluorinated compounds.^{13,14} In contrast to the ex situ analytical methods described above, chlorine photolysis and the attendant degradation chemistry were effected directly in the NMR ampule, precluding the necessity of extracting aliquots for measurement. In addition, the especially high sensitivity of ^{19}F NMR in the gas phase, which reflects very efficient spin-rotation relaxation and consequent short longitudinal relaxation times, permits the rapid acquisition of high S/N ^{19}F NMR spectra using small quantities of analyte. Moreover, the use of NMR spectroscopy enables the facile positive identification of the product species, yielding further kinetic and mechanistic insight. This method requires the use of only a standard vacuum line, a sealable NMR tube, a simple UV lamp, a NMR spectrometer, and a probe capable of ^{19}F detection.

EXPERIMENTAL SECTION

Reagents. HFCs used in this study (CF_2H_2 , CFH_2CH_3 , CF_2HCH_3 , $\text{CF}_2\text{HCF}_2\text{H}$, CF_3CFH_2 , $\text{CF}_3\text{CF}_2\text{H}$, $\text{CF}_3\text{CFHCF}_3$, $\text{CF}_3\text{CF}_2\text{CFHCFHCF}_3$) were manufactured and purified in-house to >99.9% purity by ^{19}F NMR. HFEs ($\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_2\text{HCF}_2\text{OCH}_3$, 99+%) were obtained from Synquest Laboratories and used without further purification. Chlorine (>99.9%) was obtained from GTS Gas, Inc. Ethene and propene were obtained from Phillips and Matheson Tri-Gas, respectively. Each was >99% pure by ^1H NMR. Hexafluoroethane standard was obtained and purified in house to >99.99% purity by ^{19}F NMR.

Experimental Procedure. Single-Analyte Experiments. In the single analyte experiments, a borosilicate gas-phase NMR ampule (New Era Enterprises, Vineland, NJ) was attached to a vacuum line and flame-dried with a butane–air torch. The ampule volume when sealed was 3.9 ± 0.1 mL. The ampule was then immersed in liquid nitrogen, and to it were added 1.00×10^{-5} mol of hexafluoroethane as an inert mass and chemical shift standard.

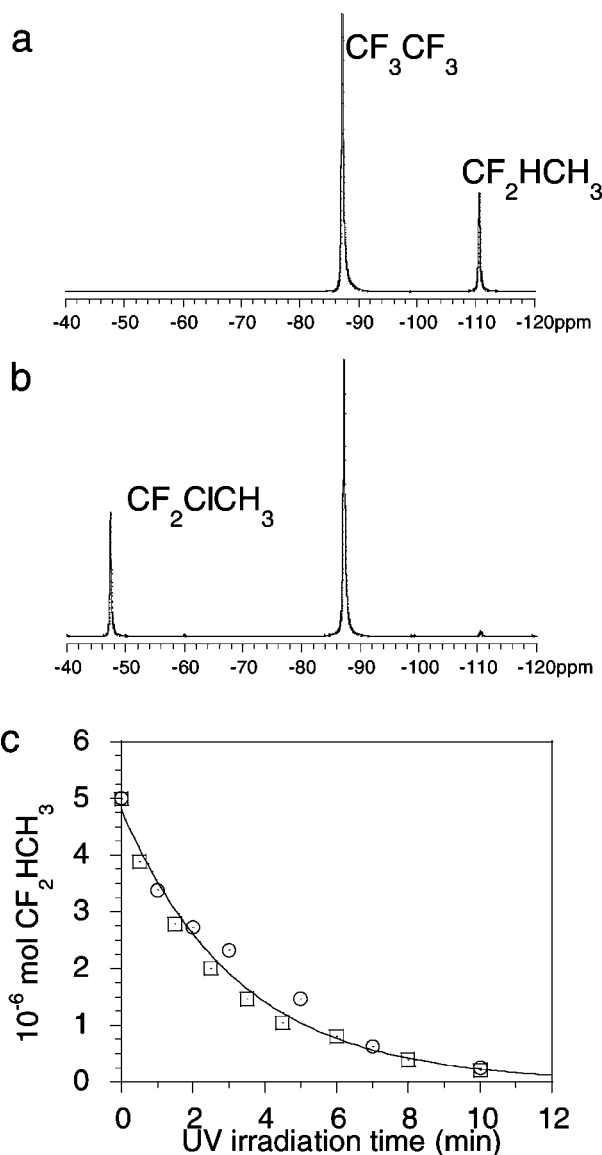


Figure 1. Results of single-analyte tests on CF_2HCH_3 . (a) ^{19}F NMR spectrum before irradiation. (b) ^{19}F NMR spectrum after irradiation. (c) Kinetic plot of $[\text{CF}_2\text{HCH}_3]$ versus irradiation time. Squares and circles indicate data from separate experiments.

The vacuum system was equipped with a Baratron barometer calibrated to ± 0.005 Torr and was of known volume and temperature; hence, quantitative molar addition of gases was achieved by means of the ideal gas law. 5.00×10^{-6} mol (typically <10 mg) analyte was transferred to the chilled ampule. Laboratory lighting was reduced to a minimum, and 1.50×10^{-4} mol of molecular chlorine was added to the ampule. The ampule was then flame-sealed and moved immediately to an opaque container. It was found that common laboratory light would effect the decomposition of many of the analytes in minutes under these conditions. At ambient temperature, the internal pressure of such ampules was 1.04 ± 0.03 bar.

The ampule was quarantined from light and inserted into the NMR probe. For the initial spectral acquisition of each compound, the longitudinal relaxation constant T_1 was measured by the inversion recovery experiment. After this, a quantitative ^{19}F NMR spectrum was acquired. The ampule was then removed from the probe and transported in the dark to an irradiation stage at a fixed

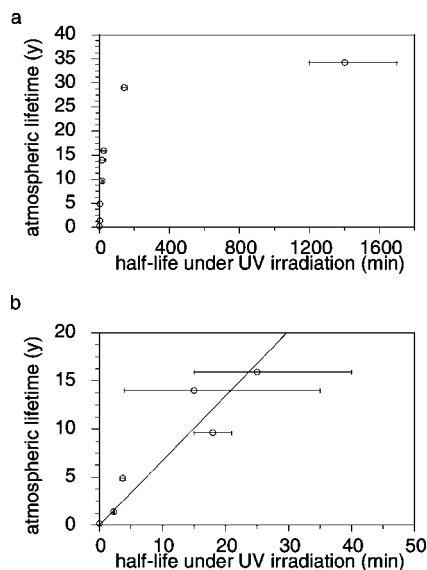
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Table 1. Half-Life Data, Accepted Atmospheric Lifetimes, and Second-Order Reaction Rate Constant with Cl[•] for Various HFCs

compound	half-life obtained (min) ^a	atmospheric lifetime (y)	JPL k (cm ³ molecule ⁻¹ s ⁻¹) ^b
CF ₂ HCH ₃	2.3 (2.3, 2.4)	1.4 ^c	2.6 × 10 ⁻¹³
CF ₃ CFH ₂	8.5 (4.8, 24)	14 ^c	1.5 × 10 ⁻¹⁵
CF ₃ CF ₂ H	1.4 × 10 ² (1.3 × 10 ² , 1.6 × 10 ²)	29 ^c	2.4 × 10 ⁻¹⁶
CFH ₂ CH ₃	4.9 × 10 ⁻² (4.3 × 10 ⁻² , 5.6 × 10 ⁻²)	0.21 ^c	6.8 × 10 ⁻¹²
CF ₂ H ₂	3.7 (3.3, 4.1)	4.9 ^d	5.0 × 10 ⁻¹⁴
CF ₂ HCF ₂ H	18 (15, 21)	9.6 ^c	2.2 × 10 ⁻¹⁵
CF ₃ CF ₂ CFHCFHCF ₃	25 (15, 40)	15.9 ^c	n/a ^f
CF ₃ CFHCF ₃	1.4 × 10 ³ (1.2 × 10 ³ , 1.7 × 10 ³) ^e	34.2 ^c	n/a

^a Values in parentheses are 95% confidence intervals. ^b Values given are second-order reaction rate constants of compound with chloro radical at 298 K. ^c From ref 19. ^d From ref 18. ^e Value given is an extrapolation from 22% decomposition (assuming pseudo-first-order kinetics) from a single experiment. ^f n/a, not applicable.

**Figure 2.** Accepted atmospheric lifetimes versus half-life under UV irradiation for HFCs. (a) Entire series plotted. (b) Expansion for compounds of lifetime <20 y.**Table 2. Relative Rate Data from Experiments with HFCs**

analyte	referent	mean k_A/k_R^a	predicted atm lifetime (y) ^a	literature atm lifetime (y) ^b
CF ₂ H ₂	CF ₂ HCH ₃	0.23 (0.22, 0.24)	6.1 (5.8, 6.4)	4.9
CFH ₂ CH ₃	CF ₂ HCH ₃	3.1 (2.8, 3.4)	0.45 (0.41, 0.51)	0.21

^a Values in parentheses are 95% confidence intervals. ^b From ref 19.

distance from a xenon arc UV lamp operating at 500 W. The light was filtered through a pinhole filter and horizontal slats before reaching the ampule; these masks combined to allow passage of only 1.8% of the incident light. A Suprasil column of purified water was circulated during irradiation in front of the lamp to prevent IR radiation from reaching and heating the test ampule. Nevertheless, the ampule did absorb some radiative energy and was warm to the touch after lengthy periods of irradiation. The effective irradiation temperature for long-scale experiments was ~30–40 °C. The UV flux at 365 nm was measured at 18 W cm⁻² by a hand-held meter from Optical Associates, Inc., before passage through the pinhole filter and slats. The extent of filtering was gauged to permit reaction rate at an acceptable scale (seconds to

minutes) for most analytes. The ampule was irradiated for a timed period and then returned to the NMR spectrometer for another quantitative spectral acquisition. The cycle was repeated until <10% of the analyte remained.

Dual-Analyte Experiments. In dual-analyte experiments, two analytes were added to the ampule instead of one, with the first serving as a reference compound for the second. Then, 5.00 × 10⁻⁶ mol of each analyte was added. The sample preparation and irradiation procedure were identical to the single-analyte experiments described above. The irradiation cycle was continued until <10% of the less stable of the analytes remained.

In the experiments with ethene and propene, no chemical shift or mass standard was added, as it was feared that any hydrogenated species might undergo some reaction with the chloro radical. Relative integration between different spectra relied on the stability of the NMR spectrometer to maintain a constant relationship between signal intensity and concentration.

NMR Spectroscopy. A photograph and a schematic of our standard gas-phase NMR experimental apparatus are provided in the Supporting Information. Gas-phase NMR experiments were performed on a Varian Unity INOVA console with a 400 MHz (9.2 T) cryomagnet. A 10-mm H–F probe from Nalorac Corp. (now Varian Inc.) was used. Spectral acquisitions were performed at 25 °C except in the case of CF₃CFHCFHCF₂CF₃, where higher temperature (70 °C) was needed to ensure complete vaporization of the analyte. T_1 relaxation measurements for each compound were made by the inversion–recovery method. Relaxation delays and acquisition times were chosen as appropriate for the analytes. Typical parameters for ¹⁹F NMR were 100 ms acquisition time and 300 ms relaxation delay (¹⁹F longitudinal relaxation in the gas phase is rapid; typical T_1 = 30 ms). Acquisitions were generally 10 min in length, averaging ~2300 transients and yielding S/N > 5000. The transmitter frequency was placed exactly between the resonances chosen for integration (an analyte resonance and hexafluoroethane for the single-analyte experiments, and a resonance for each analyte in the double-resonance experiments). Backward linear prediction of 10–20 points was applied with the Fourier transform, along with 20-Hz exponential line broadening. The chemical shifts were referenced against δ = –87.2 ppm for hexafluoroethane.

The ¹H NMR experiments carried out for the system with ethene and propene were acquired at 25 °C on the same probe. A 1.0 s acquisition time and a 17.4 s recycle delay were employed.

Table 3. Relative Rate Data from Experiments with HFEs

analyte	referent	no. experiments	mean k_A/k_R^a	predicted atm lifetime (y) ^a	literature atm lifetime (y) ^b
CF ₃ CF ₂ OCH ₃	CF ₂ HCH ₃	2	0.75 (0.69, 0.81)	1.9 (1.7, 2.0)	<5.1
CF ₂ HCF ₂ OCH ₃	CF ₂ HCH ₃	1	1.09 (1.07, 1.11)	1.28 (1.26, 1.31)	<2.6
CF ₂ HCF ₂ OCH ₃	CFH ₂ CH ₃	1	0.29 (0.18, 0.42)	0.72 (0.51, 1.17)	<2.6

^a Values in parentheses are 95% confidence intervals, ^b From ref 19.

The 32 scans were averaged and transformed with 0.5-Hz line broadening, yielding S/N > 1500.

UV-vis Spectroscopy. UV-vis experiments were performed on a Varian Cary 5000 UV-vis-NIR spectrometer. The experiments were performed directly in the test ampule, with an evacuated ampule as the reference. A typical scan rate was 60 nm/min.

RESULTS AND DISCUSSION

In attempts to model tropospheric chemistry in the laboratory, the most realistic models utilize gaseous hydroxyl radical. However, the generation of hydroxyl radicals was not easily achieved in a system compatible with NMR experiments. The generation of hydroxyl radicals by photolysis of methyl nitrite in the presence of O₂ and analyte gases was attempted.¹⁵ While radical addition to isobutylene in a test system was observed, no degradation of CF₂HCH₃ or CF₃CFH₂ was observed when they were chosen as analytes, though the methyl nitrite was completely consumed in all cases. It is believed that the concentration of the reagents necessary for an NMR study, which was higher than that reported in previous applications of this method,⁸ promoted a back-biting reaction of hydroxyl radical with methyl nitrite rather than reaction with the more stable of the analyte gases. Reaction with the surface of the ampule is another possibility, as the surface-to-volume ratio was much higher than in reported work.

Because of these difficulties, and because of the desire to develop the simplest possible analytical method, attention was focused on generation of chloro radicals by soft UV photolysis of molecular chlorine. The UV absorbance maximum of Cl₂ is at a wavelength that is readily passed by the borosilicate glass of the test ampules¹⁶ (see the Supporting Information for a UV/visible spectrum). The ampule thus permitted the unimpeded passage of UV of the appropriate wavelength for Cl₂ photolysis, while absorbing the higher-energy UV that could be responsible for photolytic degradation of analytes. A control experiment in which CFH₂CH₃ was irradiated for 2 h without pinhole filtration in the borosilicate ampule showed no degradation of the compound by ¹⁹F NMR. In the presence of Cl₂, complete degradation occurred in less than 1 min, with filters in place.

The mechanism for reaction of chloro radicals with HFCs (and saturated alkanes more generally) is well understood,¹⁷ and is given in Scheme 1. The reaction is initiated by photolysis of Cl₂ and is propagated by the abstraction of a hydrogen atom from the analyte gas. In this study, in contrast to most previous work, a large molar excess of Cl₂, not analyte, was used. This stoichiometry had two important effects: the steady-state concentration

of chloro radicals was expected to be essentially constant, permitting a pseudo-first-order kinetic analysis of the rate of analyte decomposition, and the dominant reaction for the analyte free-radical intermediate R_f[•] was likely to be the abstraction of Cl[•] from Cl₂, rather than the undesired reaction with any other free-radical intermediates. There are three conceivable termination steps—recombination of two chloro radicals (T1), combination of R_f[•] and Cl[•] (T2), and recombination of two R_f[•] radicals (T3). This last step of R_f[•] recombination would yield an “analyte dimer” product. Such dimers were not observed in the NMR spectra of any of the analytes; if present, their molar yield was <0.1%. See the Supporting Information for a more detailed treatment of the kinetics.

In such free-radical systems, the possibility of surface-assisted reactions must be considered. The experimental approach described here is not amenable to the changes in ampule material that would permit a rigorous surface study. Two brief variations of the procedure were attempted, the use of quartz rather than borosilicate ampoules before use by sealing them with excess Cl₂ and subjecting them to extended irradiation before use, in an attempt to deactivate any surface sites. Neither of these variations had any detectable effect on the reaction rates of the analytes or the product distribution. It is tentatively concluded that surface-assisted chemistry is not a significant contributor to these reactions.

Under conditions described in earlier, a set of single-analyte experiments was carried out. CF₂HCH₃, CF₃CFH₂, CF₃CF₂H, CFH₂CH₃, CF₂HCF₂H, CF₃CF₂CFHCFHCF₃, and CF₂H₂ were tested in duplicate under identical conditions. CF₃CFHCF₃ was also tested, but many hours of irradiation were required to effect even partial decomposition, and the experiment was not repeated. Figure 1 shows the results of testing of CF₂HCH₃. With this compound, there was clean conversion of the analyte to CF₂ClCH₃. This conversion illustrates the principle that fluorine atoms geminal to a given hydrogen tend to stabilize the molecule somewhat toward its abstraction, while vicinal fluorine atoms are strongly destabilizing. With all analytes, the kinetic plot of concentration versus time is fitted to an exponential decay appropriate for pseudo-first-order kinetics, and a pseudo-first-order rate constant *k* appropriate for these conditions is extracted, along with 95% confidence intervals. The goodness of fit, as measured by the square of the Pearson coefficient *R*, was greater than 0.96 for every compound but CF₃CFH₂ (0.76) and CF₃CFHCFHCF₂CF₃ (0.70). The reason for the poor fits with these latter compounds is not clear. For the purposes of establishing an empirical correlation to literature atmospheric lifetimes, a half-life of analyte decomposition was calculated from *k*. Table 1 gives the half-lives of reaction thus obtained with accepted values of atmospheric

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lifetime (obtained from the 2001 IPCC report¹⁸ or 2002 WMO report¹⁹). It is also of interest to compare the rate information obtained in this work with absolute rate data for the second-order reaction of chloro radical with HFCs collated by the NASA Jet Propulsion Laboratory.²⁰ These too are listed in Table 1.

Figure 2 plots the data given in Table 1. The top plot (a) shows all the data; the bottom plot (b) expands the data for compounds with a lifetime of <20 y and applies a linear fit. We emphasize that this is an empirical correlation; the linear fit is applied only as a simple and acceptably accurate ($R^2 = 0.87$) function relating the reaction kinetics and atmospheric lifetimes. It is not clear why approximate linearity is observed in short-lived species but not so in more stable ones. From an industrial perspective, any new volatile compounds of potential interest for large-scale manufacture would need to be short-lived and, hence, in the linear region of the plot in Figure 2.

While the results above demonstrate the utility of the method, they are limited to the particular experimental conditions chosen. Moreover, in some cases, there was significant variation in the results of replicate experiments, leading to the large confidence intervals shown on certain data points in Figure 2. This is attributed to subtle changes in the irradiation conditions (e.g., change in flux from the UV lamp, laboratory temperature), which strongly affect the kinetics of the system. A more practical and robust approach would acquire and use relative rate information. With such an approach, small quantities of both an unknown analyte and a known reference compound would be loaded in an ampule in excess Cl_2 , and the relative rates of decomposition under common irradiation conditions would be determined. In order to validate this method, a set of experiments were carried out in which two each of CF_2HCH_3 , CF_2H_2 , and CFH_2CH_3 were irradiated in excess Cl_2 . CF_2HCH_3 was chosen as the reference compound and was irradiated with each of the other analytes along a series of timed intervals in duplicate experiments. The plots of concentration versus time for each pair were fit to exponential decays, and the relative pseudo-first-order rate constants were obtained. Table 2 gives the results of this set of experiments. Using CF_2HCH_3 as a referent, and assuming an inverse linear correlation between reaction rate and atmospheric lifetime, one obtains a predicted lifetime of 0.45 y for CFH_2CH_3 (literature lifetime 0.21) and 6.1 y for CF_2H_2 (literature lifetime 4.9 y).

It is of interest to demonstrate the applicability of this method to classes of compounds other than HFCs. An obvious extension is to hydrofluoroethers, which should undergo free-radical decomposition by the same hydrogen atom abstraction mechanism. $\text{CF}_3\text{CF}_2\text{OCH}_3$ was tested in two experiments with CF_2HCH_3 as the referent, and $\text{CF}_2\text{HCF}_2\text{OCH}_3$ was tested in one experiment against CF_2HCH_3 and in another against CFH_2CH_3 . The results

are given in Table 3. According to WMO, the stratospheric degradation pathways of these ethers have not been adequately measured, and the published atmospheric lifetimes are simply upper bounds.¹⁹

A more challenging extension of this method is to olefinic species. Reaction of the chloro radical with olefins does not typically proceed by hydrogen atom abstraction. Instead, the key propagation step, addition of chloro radical to the olefin with loss of energy by collision with another molecule, is termolecular and hence pressure-dependent in a manner that the hydrogen atom abstraction pathway is not. For this reason, a valid relative rate comparison should be possible only from olefin to olefin (or other unsaturated species reacting by Cl^\bullet addition). As a brief test of the simplest olefin-to-olefin comparison, ethene and propene were chosen as analytes. An experiment proceeded as with HFCs and HFEs, but using much shorter irradiation times (fractions of a second) and using ^1H NMR detection. Under these conditions ($23 \pm 1^\circ\text{C}$, 1.0 ± 0.1 bar internal pressure), propene was found to react 1.25 times faster than ethene. The IUPAC-preferred values for the absolute rates of reaction for these compounds with Cl^\bullet at 298 K and 1 bar are $1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethene and $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for propene (2.1 times faster), and $\Delta \log k = \pm 0.3$ in both cases.²¹ The agreement of the relative reaction rate obtained with this method and that of the literature is encouraging, and supports our belief that this method should be applicable to unsaturated species as well.

CONCLUSIONS

A method of estimating atmospheric lifetimes by chlorine photolysis as measured by gas-phase NMR has been described. The estimates so generated are only approximate measures of the true lifetimes. Nevertheless, the method is sufficiently accurate to serve as a "quick screen", which is readily applicable early in the process of consideration of a new industrial product. As the method requires only a vacuum line, a UV lamp, a sealable NMR tube, and a NMR probe capable of ^{19}F (or ^1H) detection, it is applicable in most ordinary synthetic chemical laboratories. Even the practice of flame sealing, facile in our laboratories, can be obviated by use of commercially available valved NMR tubes. Moreover, a duplicate set of experiments can be completed in a day's time with only milligrams of analyte, rendering the method fast and inexpensive.

The use of NMR detection in the gas phase may be applicable to more sophisticated indirect rate measurements. NMR intrinsically provides structural information beyond that furnished by GC, IR, or even mass spectrometric techniques. Moreover, particularly for fluorinated compounds, the efficient relaxation processes, and attendant fast pulse repetition rate in the gas phase, yield greater sensitivity than is typically appreciated for quantitative NMR studies.

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SUPPORTING INFORMATION AVAILABLE

Photograph and schematic of our standard gas-phase NMR experimental apparatus, UV/visible spectra of empty ampule and ampule charged with Cl_2 , gas-phase NMR data and comprehensive

kinetic analysis of the reaction of HFCs with Cl^\bullet . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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