visible detection would be difficult. Laser flash photolysis with infrared detection on the other hand does not suffer from the same disadvantages in that strong IR bands corresponding to carbonyl stretching transitions are accessible for all of the species involved with no overlap of the expected absorbances, i.e., for **1**, 1750 cm^{-1}; for **2**, 2129 and 1690 cm^{-1}; and for **3**, 1850 cm^{-1}.[7] LFP-TRIR experiments[11] were carried out using 308-nm excitation on a 3 × 10^{-3} M solution of **1** in cyclohexane. LFP-TRIR spectra, obtained 200 ns after the 308-nm laser pulse and every 1.0 μs thereafter for 4.2 μs, are shown in a 3D representation in Figure 1. Three distinct transient features are observable in these spectra, formation of two new absorbances and the bleaching of the precursor. The kinetic traces associated with each of the phenomena are shown in Figure 2. Panel A depicts the kinetic trace recorded at 1690 cm^{-1}, monitoring the absorption that we assign to the aldehyde stretch of **2**.[15] It decays with first-order kinetics with a lifetime of 2.9 μs. Similarly, panel B shows the bleaching and partial recovery of **1** monitored at 1750 cm^{-1}. The rate of the recovery is consistent with the rate of decay of **2**. The short ketene lifetime and the extent to which the bleaching recovers suggests that the thermal reversion of **2** back to **1** is both rapid and efficient. Finally, panel C shows the kinetic trace obtained at 1850 cm^{-1} corresponding to an absorption that is assigned to **3**. There is no doubt that **3** is formed instantaneously on our time scale, eliminating the possibility that it is formed thermally from **2**. The intensities of the absorptions at 1690 and 1850 cm^{-1} (as well as that of the bleaching at 1750 cm^{-1}) increase linearly with the laser flux, proving that both **2** and **3** are primary photoproducts from **1**. The quantum yields for their formation were determined to be $\Phi_2 = 0.52 \pm 0.1$ and $\Phi_3 = 0.09 \pm 0.1$, respectively, by comparing the intensity of the bleaching at 1750 cm^{-1} with the intensity of the absorption obtained for a standard reaction under otherwise identical conditions.[16]

The addition of small quantities of methanol leads to a decrease in the observed optical density of the 1690-cm^{-1} absorption assigned to **2**, but its rate of decay remains unchanged. This type of behavior is characteristic of the scavenging of an early intermediate, which in this case must be the singlet excited state of **1**.[17] The LFP-TRIR spectrum obtained for a cyclohexane solution containing sufficient methanol to completely inhibit formation of **2** shows only instantaneous permanent bleaching of the absorption assigned to **1** and the instantaneous formation of a new absorption that does not decay within the time scale of our experiment. This absorption, at 1715 cm^{-1}, is assigned to the cyclic addition product **4** on the basis of the reported carbonyl stretching frequencies of the dimethyl derivative.[9] The other expected product, **5**, should absorb at ~1755 cm^{-1}, which is close to where bleaching of **1** occurs. A ~10-cm^{-1} shift to lower wavenumber in the bleaching maximum and its much smaller intensity compared with that observed in the absence of methanol indicate that **5** is indeed formed but its absorbance is masked by the bleaching of **1**. The open ester product, $CH_3OC(O)CH_2CH{=}CHCHO$, expected if **2** were to react with methanol, has two carbonyl stretching vibrations at 1733 (ester) and 1686 cm^{-1} (aldehyde).[5] These absorptions are absent in our experiment. This indicates that, in solution, methanol quenches the singlet excited state of **1** in preference to reacting with **2**.

In summary, we have unequivocally shown that ketene **2** and the lactone **3** are both primary products of the photochemical reaction of 2*H*-pyran-2-one (**1**). Furthermore, we have provided strong evidence that the excited singlet state of **1**, and not ketene, is responsible for the observed photoreactivity with methanol. The ketene has a lifetime of only 2.9 μs in solution at 25 °C, and it reverts efficiently back to the starting pyrone in an energy-wasting process.

These studies show the versatility of infrared detection of transients since vibrational transitions are more sensitive to molecular structure than are electronic transitions. Further studies concerning the reactivity of 2*H*-pyran-2-one and similar sources of ketenes are planned.

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(11) The LFP-TRIR apparatus used has been described elsewhere.[12-14] Further experimental details will be published with the full report of this work.

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(15) The absorption at 2129 cm^{-1}, attributable to $C{=}C{=}O$ stretch of **2**, and the UV band at 295 nm are also observable in solution and display similar kinetics.

(16) We have chosen the decarbonylation of diphenylcyclopropenone as our standard reaction, which was itself calibrated against the benzophenone/piperylene actinometer using 308-nm laser pulses from a Lumonics EX-500 excimer laser. The quantum yield for the decarbonylation was determined to be $\Phi = 1.00 \pm 0.03$. Product formation and starting material depletion were followed using GC analysis. Extinction coefficients were determined using a Nicolet 20DBX FTIR spectrometer. The relative values reported for the quantum yields are known much more accurately than the reported error limits imply. The large error in the absolute values is due to uncertainties in the infrared extinction coefficients and the determination of the observation wavelength, as well as the usual errors associated with quantum yield determinations using lasers as radiation sources. Experimental details will be published with the full report of this work.

(17) The yield of the ketene is not affected by addition of typical triplet quenchers, such as biacetyl.

Alkene Reactivities toward a Strongly Electrophilic Radical. First Absolute Rate Constants for Some Reactions of Perfluoro-*n*-alkyl Radicals in Solution[1]

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The absolute reactivities of alkyl and perfluoroalkyl radicals are expected to differ significantly since the former are electron-rich, planar π-radicals, whereas the latter are electron-poor, nonplanar σ-radicals. Direct, time-resolved methods have been extensively employed to obtain absolute kinetic data for a wide variety of alkyl radical reactions in the liquid phase,[3] but no such measurements have been made for perfluoroalkyl radicals. Indeed, even relative rate data for fluoroalkyl and other electrophilic radicals in solution are sparse.[3,4] Since the effective use of fluoroalkyl radicals in organic synthesis requires a proper understanding of their reactivity vis-à-vis the reactivity of structurally related alkyl radicals, we have begun a program to measure the absolute kinetics of prototypical fluoroalkyl radical reactions by a combination of laser flash photolysis (LFP), product analyses, and conventional competitive kinetics. The stereoelectronic factors governing the reactivity of nucleophilic alkyl radicals, particularly in addition reactions, have been extensively examined.[5-8] There

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(2) NRCC Research Associate, 1991–1992.

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Table I. Absolute Rate Constants for Some Reactions of Perfluoro-*n*-alkyl and *n*-Alkyl Radicals in Solution at 298 ± 2 K[a]

substrate	$k^{n\text{-}C_3F_7\cdot}/10^6$ M^{-1} s^{-1} k_{gl}	k_{add}	k_{abs}	$k^{RCH_2CH_2\cdot}/10^3$ M^{-1} s^{-1} k_{gl}	IP/eV[h]
1. $C_6H_5CH{=}CHCH_3$	3.8 ± 0.2	3.8			
2. $C_6H_5C(CH_3){=}CH_2$	79 ± 8	79		59[b]	8.20[f]
3. $C_6H_5CH{=}CH_2$	43 ± 1	43		120[b]	8.40
4. $H_2C{=}\overline{C(CH_2)_2C({=}CH_2)CH_2C}H_2$	41 ± 3	41[g]		0.13[c,d]	9.12[g]
5. $H_2C{=}CH(CH_2)_3CH_3$	6.2 ± 0.2	6.2		0.2[c,e]	9.31
6. $H_2C{=}CCl_2$	5.2 ± 0.3	5.2			10.0
7. $H_2C{=}CHC(CH_3)_2OH$	2.8 ± 0.3	2.8			9.90
8. $H_2C{=}CHCN$	2.2 ± 0.1	2.2			10.92
9. $H\overline{C{=}CH(CH_2)_3C}H_2$	1.29 ± 0.05	1.2	0.09		

[a] Errors correspond to 2σ but include only random errors. [b] From ref 21 as modified for temperature and other factors in Table III of ref 22. [c] From ref 3, Part a, p 160. [d] Reaction is $C_2H_5\cdot + H_2C{=}C(CH_3)_2 \rightarrow C_3H_7C\cdot(CH_3)_2$. [e] Addition of $C_2H_5\cdot$. [f] The IP of α-methylstyrene does not reflect its HOMO energy in the transition state because, in the ground state, the double bond is twisted out of the phenyl ring plane.[23] In the transition state the phenyl ring will be coplanar with the incipient benzyl radical center. [g] IP taken as for methylenecyclohexane and log ($0.5k_{add}$) used in the of plot log k_{add} vs IP. [h] The IPs are taken from ref 24.

is, however, no similar information available for strongly electrophilic carbon-centered radicals.

The perfluoro-*n*-propyl radical was generated "instantaneously" by 308-nm LFP of the parent diacyl peroxide (ca. 0.16 M)[9] in $CFCl_2CF_2Cl$ at room temperature, and its rate constants for the "global" reactions, k_{gl}, with some styrenes were obtained using standard LFP techniques.[10] The rate constants for the global reactions of $n\text{-}C_3F_7\cdot$ with olefins that do not form easily observed products, i.e., 1,4-dimethylenecyclohexane, 1-hexene, 1,1-dichloroethylene, 2-methyl-3-buten-2-ol, acrylonitrile, and cyclohexene, were also measured by LFP at ambient temperature using 0.11 M β-methylstyrene as a "probe".[10,11] All of the kinetic data are summarized in Table I.

To determine what fraction of k_{gl} for the methyl styrenes should be assigned to addition, k_{add}, and what fraction assigned to possible H-atom abstraction reactions, k_{abs}, α-methyl- and β-methylstyrene in separate experiments were reacted with $n\text{-}C_4F_9I$[12] in degassed cyclohexane at room temperature under radical-chain conditions (initiation by UV irradiation, 10 h). The products were analyzed quantitatively by ^{19}F NMR using $C_6H_5CF_3$ as an internal standard. No $n\text{-}C_4F_9H$ was formed; the only product in each case was that of 1:1 addition, $C_4F_9CH(R)C(I)R'C_6H_5$ (R = H, CH_3). We can therefore equate k_{gl} with k_{add} for all three styrenes. In a rather similar experiment with $n\text{-}C_4F_9I$ and cyclohexene (AIBN initiated, 60 °C, 50 h), only 7.2% of the H-abstraction product, $n\text{-}C_4F_9H$, was obtained.[13] Since all of the other substrates examined are terminal alkenes and since most do not contain allylic H-atoms, it appears safe to assume that H-abstraction from them can be neglected.[14] We therefore equate k_{gl} with k_{add} for all of the olefins studied except cyclohexene (see Table I).

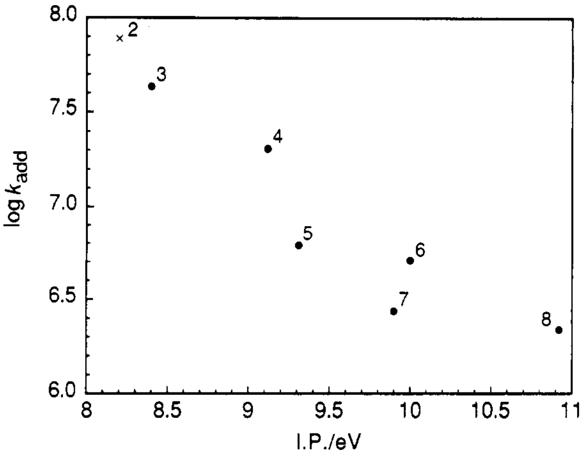

Figure 1. Plot of the log of the rate constants for addition of the perfluoro-*n*-propyl radical to some alkenes vs ionization potentials of the alkenes. Because the IP for **2** does not reflect the transition-state HOMO (see footnote f in Table I), this point has been indicated by an ×.

Perfluoro-*n*-alkyls are much more reactive than *n*-alkyl radicals in addition reactions (note the change in scaling factors in Table I). This difference in reactivity cannot be attributed to a much greater enthalpic driving force for the perfluoroalkyl additions since the available evidence suggests that the primary C–H bond dissociation energies for $C_nF_{2n+1}H$ and C_nH_{2n+2} are rather similar.[15] Following earlier suggestions,[4b,j,5,6] we therefore attribute the enhanced reactivity of the electron-poor perfluoro-*n*-alkyl radicals to polar factors which act to stabilize an early transition state, i.e., $[(C_3F_7\cdot)^{\delta-}(\text{substrate})^{\delta+}]^{\ddagger}$, and thus act to lower the enthalpic barrier for their reactions with electron-rich olefins.[17] The enthalpic barrier for reactions will also be decreased by polar contributions of the transition state.[18]

The rather small rate-accelerating effect observed when an alkyl group is replaced by phenyl provides evidence for an early transition state in these additions. The geometries of the (early) transition states for addition of "nucleophilic" and "electrophilic" radicals to alkenes should be rather similar.[19] However, these

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(9) This concentration gave an OD of ~0.3 at 308 nm in a 7-mm cell.

(10) That is, via monitoring the pseudo-first-order growth of the ca. 320-nm absorption due to the resulting benzylic radical: $n\text{-}C_3F_7\cdot + RCH{=}CR'C_6H_5 \rightarrow n\text{-}C_3F_7CH(R)C\cdot R'C_6H_5$ (R, R' = H; R = H, R' = CH_3; R = CH_3, R' = H). The rate constants for the "global" reactions of $n\text{-}C_3F_7\cdot$ with the styrenes, k_{gl}, were calculated from the experimental growth curves measured over a range of substrate concentrations, i.e., $k_{exptl} = k_0 + k_{gl}[RCH{=}CR'C_6H_5]$. The equation, k_{exptl} (320 nm) $= k_0 + k_\beta[CH_3CH{=}CHC_6H_5] + k_{gl}[\text{substrate}] = k_0' + k_{gl}[\text{substrate}]$, was applied for the probe measurements.

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(12) The *n*-perfluorobutyl iodide was used instead of the *n*-perfluoropropyl iodide because it was available in the lab. The reactivities of the respective radicals should be identical.

(13) After a mixture of cyclohexene (2.5 mmol), $n\text{-}C_4F_9I$ (0.42 mmol), and AIBN (6 mg) was heated at 60 °C for 50 h, it was found that 4.1% of $n\text{-}C_4F_9H$, 47.6% of the 1:1 addition product, and 5.6% of other $n\text{-}C_4F_9$-containing products were formed and 40.5% $n\text{-}C_4F_9I$ was recovered.

(14) The two terminal olefins which do contain allylic H-atoms are both much more reactive than cyclohexene ($k_{abs} = 0.07k_{gl}$), which strongly implies that H-abstraction is of negligible importance.

(15) For example,[16] $D[C_2F_5\text{–}H]$ = 102.7 ± 0.5 and $D[C_2H_5\text{–}H]$ = 100.3 ± 1.0 kcal/mol.

(16) Kerr, J. A. In *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991–92; pp 9, 114–117.

(17) We anticipate that perfluoroalkyls will be less reactive than the corresponding alkyl radicals toward electron-poor olefins and electron-poor atom donors (e.g., CCl_4). Experiments are underway which should put these qualitative concepts onto a quantitative footing which will have predictive value.

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(19) Giese, B.; He, J.; Houk, K. N.; Zipse, H. *J. Am. Chem. Soc.* **1991**, *113*, 4324–4325.

two classes of radicals would be expected to show opposite trends in their reactivities toward electron-rich and electron-poor alkenes. In this connection, Fischer et al.[20] have shown that the rate of addition of the nucleophilic *tert*-butyl radical (which has a high-lying SOMO, IP = 6.7 eV) tends to increase with an increase in electron affinity of the alkene, a result which indicates that the SOMO–LUMO interaction is important for these reactions. By way of contrast, it is the SOMO–HOMO interaction which should dominate the addition of the strongly electrophilic radical, n-$C_3F_7^{\bullet}$, to alkenes. This is demonstrated by the rough correlation ($\langle r\rangle = 0.94$) between log k_{add} and IP for the seven terminal alkenes shown in Figure 1. This correlation is about as good as that of Fischer et al.[20] for log $k_{add}(Me_3C^{\bullet} + \text{alkenes})$ vs electron affinity ($\langle r\rangle = 0.89$) for a series of 21 alkenes. In both systems there are substantial deviations from the best straight line, which indicate that additional factors must control the reaction rates.[25] Experiments are underway to try to discover some of these "complicating" factors.

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(24) Levin, R. D.; Lias, S. G. *National Bureau of Standards: Ionization Potential and Appearance Potential Measurements, 1971–1981*; U.S. Government Printing Office: Washington, DC, 1982.

(25) Ambiphilic behavior has been observed for the addition of two somewhat less electrophilic radicals, viz., $PhCH_2\dot{C}(CO_2Et)_2$[4j] and $Me_3COC(O)\dot{C}H_2$,[4k] to alkenes with distinct minima in plots of log(k/M^{-1} s^{-1}) vs. alkene IP.

Complete Sideband Suppression in Magic Angle Spinning Solid-State Nuclear Magnetic Resonance for Arbitrary Chemical Shift Anisotropies

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Magic angle spinning (MAS)[1,2] has become an indispensable method for obtaining high-resolution NMR spectra of dilute spins in solids. For spin-$^1/_2$ nuclei, the effect of MAS depends on the ratio $a = \omega_0\Delta\sigma/\omega_r$, where $\Delta\sigma = \sigma_{33} - \sigma_{iso}$ is the anisotropy of the chemical shift tensor, ω_0 the Larmor frequency, and ω_r the spinning frequency.[3,4] Fast MAS ($a \ll 1$) causes the static powder lineshape to collapse into a single resonance at the isotropic chemical shift $\omega_0\sigma_{iso}$. However, high spinning speeds present technical difficulties, may degrade cross polarization,[5,6] and also require small sample volumes. Slow MAS ($a > 1$) results in spinning sidebands at $\omega_0\sigma_{iso} \pm n\omega_r$ which often impair resolution. TOSS[7–10] (total sideband suppression) sequences have therefore been devised that achieve sideband cancellation for isotropic powder samples. However, TOSS also attenuates the centerband,[8,10,11] giving a residual centerband containing only 50% of the full intensity at $a \approx 2.5$ and zero intensity at $a \approx 4.5$, for $\eta = (\sigma_{22} - \sigma_{11})/\Delta\sigma = 1$. Here we present a new sideband suppression experiment which gives centerbands containing 100% of the full intensity *irrespective of the ratio a.*

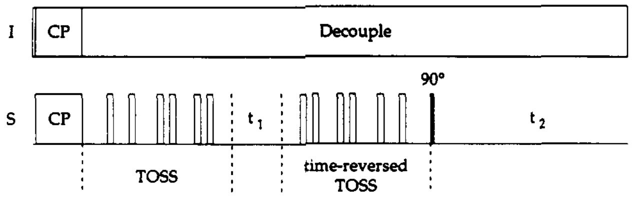

Figure 1. Pulse sequence for a MAS sideband suppression experiment for arbitrary ratios $a = \omega_0\Delta\sigma/\omega_r$. Cross polarization is followed by TOSS, an evolution period t_1, and then time-reversed TOSS. A 90° purging pulse selects one component of the magnetization for detection.

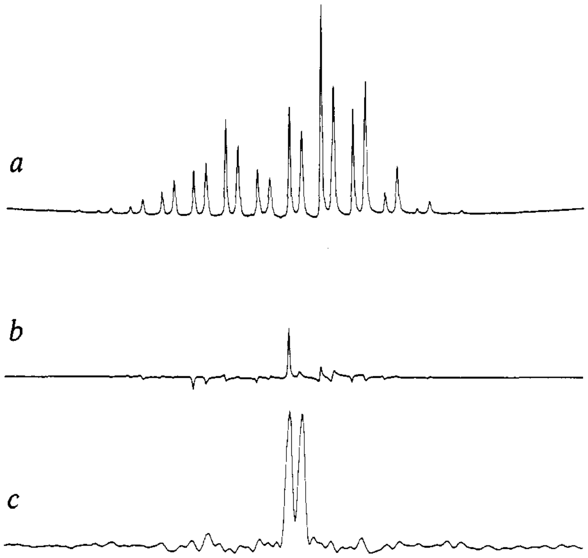

Figure 2. ^{31}P spectra of magnesium pyrophosphate, $Mg_2P_2O_7$, with a spectral width of 37.8 kHz at 121.5 MHz and $\omega_r/2\pi = 2$ kHz. (a) Normal MAS spectrum. (b) TOSS spectrum obtained with the six-pulse sequence of Raleigh et al.[9] The centerbands are strongly attenuated since $a = \omega_0\Delta\sigma/\omega_r \gg 1$. (c) Spectrum recorded with the method of Figure 1. Here the isotropic peaks have equal areas since each contains the full MAS intensity of the corresponding sideband family.

The new method is shown in Figure 1, for dilute spins-$^1/_2$ S (such as ^{13}C or ^{31}P) coupled to abundant spins I (such as ^1H). We have demonstrated[12] that evolution under the [TOSS–t_1–reverse TOSS] sequence[13] is governed by the isotropic part of the chemical shift Hamiltonian alone and is thus independent of a. Therefore, the phase accumulated by the magnetization between the excitation sequence and the purging pulse of Figure 1 is $\varphi = \omega_0\sigma_{iso}t_1$, giving a signal immediately after the purging pulse proportional to cos φ, irrespective of the orientational distribution of crystallites. By stepping t_1 in the manner of a two-dimensional experiment, with increments Δt_1 small enough to sample the range of isotropic chemical shifts, and by using time-proportional phase increments (TPPI) to shift the origin of the frequency domain,[14,15] one can monitor the modulation indirectly through the amplitude of the first data point acquired. A real Fourier transformation

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