Photochemistry of Hexafluoroacetone Imine[1]

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Abstract: Hexafluoroacetone imine (Im) was photolyzed at 254 nm in the range 3-100 Torr, 25-300°. The effects of added O_2, C_2H_4, and n-C_6H_{14} were also investigated. The major product was CF_3CN with smaller amounts of CF_3H and H_2. Trace quantities of CO_2 were found but C_2F_6 could not be positively identified in the products. A slow thermal decomposition occurred at 300°. The small values of $\Phi(CF_3CN)$ ($<10^{-3}$ at 25° and 50 Torr) indicated efficient collisional deactivation. Plots of Φ^{-1} *vs.* [Im] are curved but plots of $\Phi/(1-\Phi)$ *vs.* $[\mathrm{Im}]^{-1}$ are linear with slopes and intercepts which increase with temperature. The results are interpreted in terms of decomposition from both excited singlet and triplet states. Added O_2 increased $\Phi(CF_3CN)$ but decreased $\Phi(CF_3H)$ and this is accounted for by postulating a reaction between O_2 and triplet Im. Both C_2H_4 and n-C_6H_{14} decreased all products. CF_3 radicals were shown to undergo addition to Im much more rapidly than they abstract H atoms.

The photochemistry of hexafluoroacetone has been extensively investigated[3] and the main primary and secondary processes have been well established. The molecule is of interest both as a model system for electronic energy conversion and as a convenient source of CF_3 radicals.[4]

Hexafluoroacetone imine, $(CF_3)_2CNH$, isoelectronic with hexafluoroacetone, has become available.[5] The $n\pi^*$ band in the alkyl ketones has a maximum at about 280 nm ($\epsilon \sim 14$) which is shifted to 300 nm (ϵ 8) for hexafluoroacetone. In the case of hexafluoroacetone imine the maximum occurs at 247 nm and is far more intense (ϵ 94.5). As recently described,[6] the positions of the maximum and minimum in the absorption spectrum make the imine a convenient filter for removing 254-nm radiation and passing 185-nm light.

We decided to make a study of the imine, expecting the photochemistry to be rather similar to that of hexafluoroacetone. However, the results showed that although the primary processes showed similarities, the secondary photochemistry was quite different.

Experimental Section

A mercury-free vacuum system was used with greaseless stopcocks in sections exposed to reactant or products. The cylindrical quartz photolysis cell, 4.8 cm in diameter, 10.2 cm long, was enclosed in an aluminum block furnace which was thermostated to within ±0.5°.

A low-pressure mercury vapor lamp[7] powered by a 7500-V transformer was the light source. The electrodes were water cooled, and a getter was employed to remove possible traces of oxygen. The output of this lamp as measured by a $^1/_4$ m Jarrell Ash monochromator and 1P28 photomultiplier is shown in Figure 1. Also shown is the absorption spectrum of the imine measured with a Cary 15 spectrophotometer. Virtually all of the absorbed light is from the 254-nm line. In the photolysis system the transmitted light was monitored by an RCA 935 photodiode. Intensity was varied using quartz neutral density filters and conversions were kept <1%.

Actinometry was carried out with hydrogen bromide[8] using small photolytic conversions and assuming the quantum yield of hydrogen $\Phi(H_2) = 1$. The hydrogen was measured by freezing out Br_2 and HBr at −196° and reading the residual hydrogen pressure on a thermocouple gauge which had been calibrated for hydrogen. Blanks with added hydrogen showed this simple procedure to be quantitative. A Beer–Lambert plot gave the decadic extinction coefficient of HBr to be 0.97 l. mol^{-1} cm^{-1} at 254 nm and 25°.

Hexafluoroacetone imine (from Columbia Organic Chemicals Co., Columbia, S. C.) was triple distilled and no impurities were found by gas chromatography. Research grade n-C_6F_{14}, C_2H_4, and commercial O_2 were distilled before used.

Products condensable at −196° were analyzed by gas chromatography using a silica gel column at 65° and also with a mass spectrometer (Finnegan Instruments Corp.). Unreacted imine eluted from the silica gel column at 150°. A small amount of a noncondensable product was consistently found in the photochemical decomposition. This substance was not the vapor of a condensed product and could be evacuated very rapidly from the photolysis cell. The only possibilities were H_2 and N_2, and since the latter is not a feasible product from an imine we assumed the noncondensable product was H_2..

The sensitivity of the chromatograph to CF_3CN was found to vary appreciably, necessitating the frequent use of standards. Chromatograph difficulties with nitriles have been noted by other workers.[9]

Results

Physical Properties of Hexafluoroacetone Imine. The vapor pressure was measured from −47 to −19° and obeyed the relation $\log P_{\mathrm{Torr}} = -(1970 \pm 25)/T°\mathrm{K} + 9.79$, which gives $\Delta H_v = 9.0 \pm 0.1$ kcal mol^{-1}.

The absorption spectrum of the imine is given in Figure 1. At 254 nm, linear Beer–Lambert plots were obtained at 25, 100, and 200° with a decadic extinction coefficient of 87.5 ± 1.0 at each temperature.

The mass spectrum has not been previously reported and is given in Table I. It is interesting to note that one of the largest peaks is due to CF_2H^+, an ion formed by rearrangement. A similar effect has been noted in the fluoroaldehydes.[10]

Photolysis Results. Photolysis of the imine alone was carried out in the range 25–300°, 3–100 Torr. The major product was always CF_3CN, with smaller

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[2] (a) University of California; (b) Rutgers University.

[3] See, for example, A. Gandini, D. A. Whytock, and K. O. Kutschke, *Proc. Roy. Soc., Ser. A*, **306**, 541 (1968); P. G. Bowers, *Can. J. Chem.*, **46**, 307 (1968); J. S. E. McIntosh and G. B. Porter, *J. Chem. Phys.*, **48**, 5475 (1968); W. R. Ware and S. K. Lee, *ibid.*, **49**, 217 (1968), and references cited therein.

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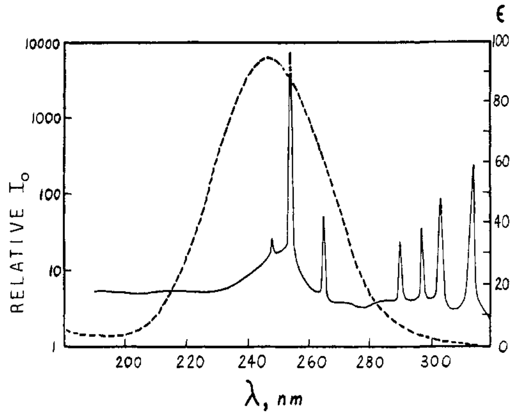

Figure 1. Emission spectrum of low-pressure mercury lamp (solid line, left ordinate) and absorption spectrum of hexafluoroacetone imine (dashed line, right ordinate, ε in l. mol^{-1} cm^{-1}).

amounts of H_2 and CF_3H. No C_2F_6 was ever found (an approximate upper limit for $\Phi(C_2F_6)$ was 10^{-5}), but traces of CO_2 were occasionally detected. We did not analyze quantitatively for heavy addition products but mass spectral peaks at *m*/*e* >300 confirmed their formation. The mass spectra were scanned for HCN and although its occurrence could not be entirely ruled out, it was clear that HCN, if formed, was a minor product. The possibility of a large amount of dimerization was checked by measuring the total pressure before and after photolysis for several runs. No significant differences were found. However, it was noticed that a white polymeric material was formed in the "cold finger" attached to the photolysis cell. This polymer was heated and pumped away occasionally.

Table I. Mass Spectrum of Hexafluoroacetone Imine (70 eV)

m/*e*	Assigned ion	Intensity	*m*/*e*	Assigned ion	Intensity
165	$(CF_3)_2CNH$	0.2	58	CFCNH	0.8
147	*a*	0.2	57	CFCN	0.3
146	CF_2CF_3CNH	2.8	52	*a*	0.4
119	C_2F_5	0.2	51	CF_2H	34.4
100	C_2F_4	0.4	50	CF_2	15.1
97	*a*	2.6	46	FCNH	1.3
96	CF_3CNH	100.0	43	C_2F	0.2
95	CF_3CN	0.3	38	C_2N	0.2
93	CF_3C_2	0.4	32	CFH	0.5
81	CF_3C	0.2	31	CF	9.0
78	*a*	0.2	27	CNH	1.8
77	CF_2CNH	5.9	26	CN	0.2
76	CF_2CN	2.1	20	HF	0.2
74	CF_2C_2	0.2	19	F	0.2
70	*a*	1.0	15	NH	0.2
69	CF_3	91.8	12	C	0.4
62	CF_2C	0.2			

[a] Isotope peak.

The quantum yields of the measured products are plotted as a function of imine pressure in Figures 2–5. Included at 200° are some runs with added *n*-C_6F_{14}. At 300° a small dark reaction was apparent. In the thermal decomposition no H_2 was formed but traces of CF_3H and CO_2 were detected. CF_3CN was formed thermally to the extent of 3% of the photolytic reaction at 12 Torr and 14% at 100 Torr. Figure 5 is corrected for the thermal reaction.

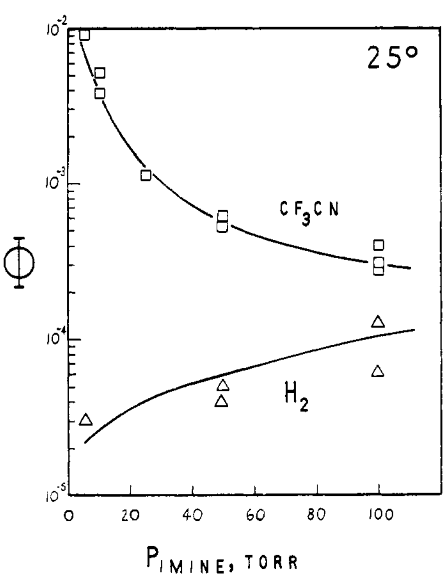

Figure 2. Quantum yields of products as a function of imine pressure at 25°; semilogarithmic plot.

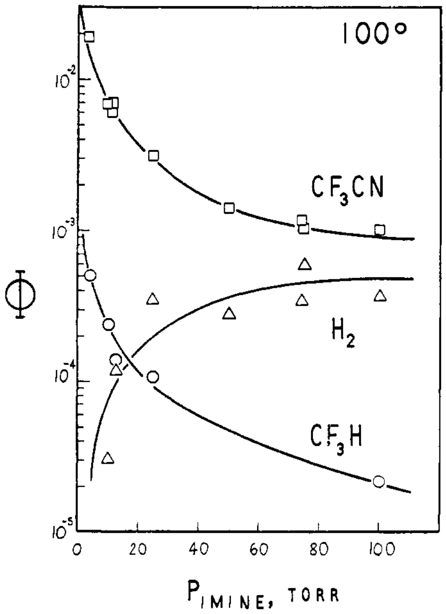

Figure 3. Quantum yields of products as a function of imine pressure at 100°; semilogarithmic plot.

The effect on quantum yields of a 12-fold change in incident intensity at 200° and 10 Torr of imine is shown in Figure 6.

The results of experiments with varying amounts of added oxygen at 25 and 200° are shown in Figure 7. Oxygen scavenged CF_3H from the products but it was not possible to determine whether H_2 was formed in the presence of O_2. At both temperatures the presence of O_2 led to an increase in $\Phi(CF_3CN)$ and resulted in the formation of CO_2 as a major product. Chromatograms also showed some small unidentified peaks from runs in the presence of oxygen.

A series of runs at 200°, 10 Torr of imine, was carried out in the presence of ethylene. It was found that H_2 and CF_3H could not be detected in the products and $\Phi(CF_3CN)$ showed a marked decrease. This is illustrated in Figure 8.

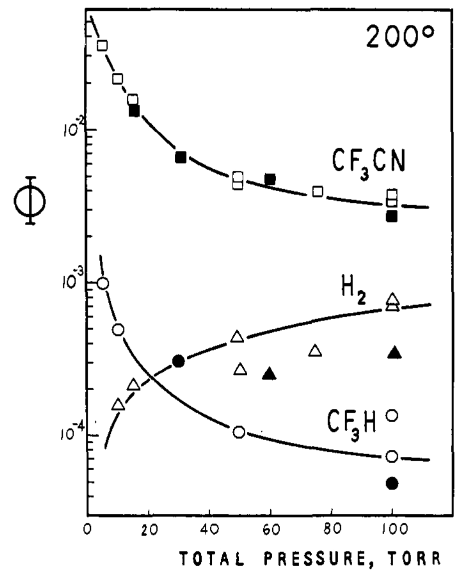

Figure 4. Quantum yields of products as a function of total pressure at 200°: unfilled points, pure imine; filled points, 10 Torr of imine + n-C_6F_{14}; semilogarithmic plot.

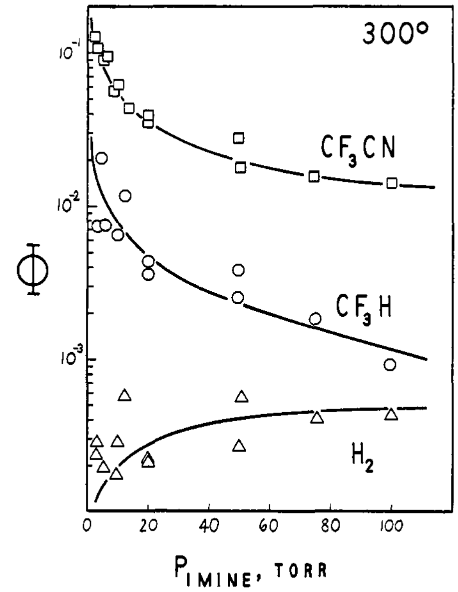

Figure 5. Quantum yields of products as a function of imine pressure of 300°; semilogarithmic plot.

An attempt was made to measure the luminescence emitted by the imine when irradiated with 248-nm light using a monochromator. No emission was seen in the scanned region of 280–600 nm, nor within the scatter peak of the excitation light. A comparison with biacetyl made it possible to set an upper limit for imine emission of $\phi \leqslant 6.5 \times 10^{-6}$.

Discussion

Primary Processes. The rapid decrease of $\Phi(CF_3CN)$ as imine pressure increases indicates considerable collisional deactivation. The range of $\Phi(CF_3CN)$ was from 3×10^{-4} at 100 Torr, 25°, to 0.12 at 3 Torr, 300°. Plots of Φ^{-1} (where $\Phi = \Phi(CF_3CN)$) *vs.* imine pressure show curvature at all temperatures. The data are insufficient to indicate whether or not the intercept is unity. On the other hand, plots of $\Phi/(1 - \Phi)$ *vs.* the

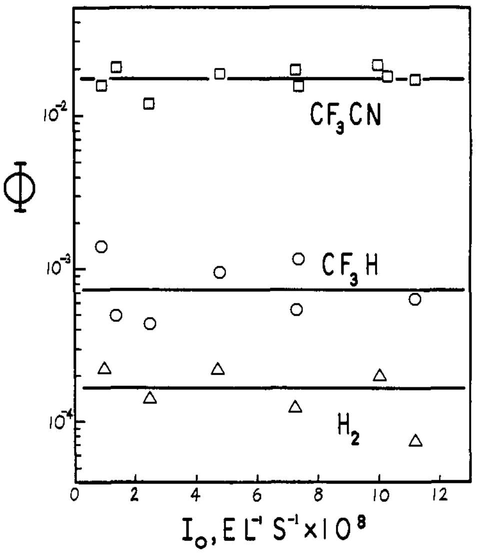

Figure 6. Quantum yields of products as a function of incident intensity at 200° and 10 Torr of imine; semilogarithmic plot.

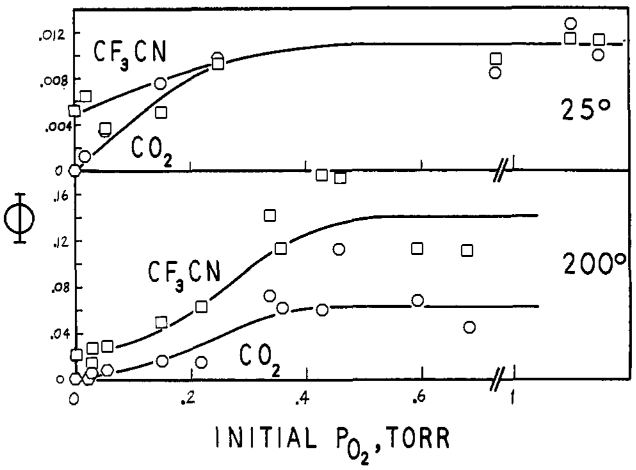

Figure 7. Quantum yields of products as a function of added oxygen at 10 Torr of imine at 25 and 200°.

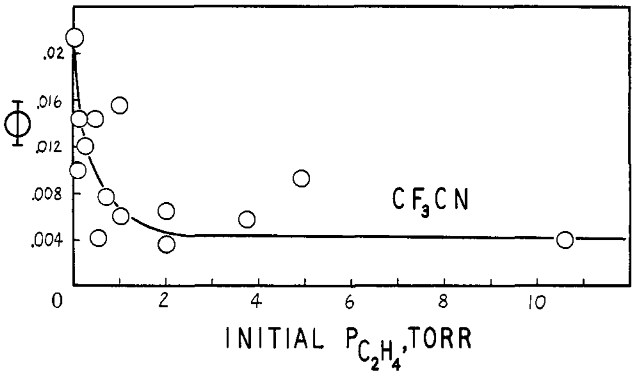

Figure 8. Quantum yield of product as a function of added ethylene at 10 Torr of imine and 200°.

reciprocal of imine pressure are linear as seen in Figure 9, with the possible exception of a point at 300° and low pressures. Ignoring the small anomaly this behavior is similar to that of hexafluoroacetone[3] and is consistent with decomposition from two excited states. The following mechanism is proposed.

Table II. Ratios of Rate Constants of Primary Processes

	25°	100°	200°	300°
k_2/k_1, l. mol^{-1}	6.4×10^5	3.3×10^5	1.6×10^5	1.0×10^5
$k_1/(k_2 - k)$, mol l.$^{-1}$	2.6×10^{-6}	2.8×10^{-6}	6.1×10^{-6}	13×10^{-6}
k/k_2	2.5×10^{-4}	7×10^{-4}	3×10^{-3}	1×10^{-2}

$$\mathrm{Im} + h\nu \longrightarrow {}^1\mathrm{Im}^n \tag{0}$$

$$^1\mathrm{Im}^n \longrightarrow \mathrm{CF_3CN} + \mathrm{CF_3H} \tag{1}$$

$$^1\mathrm{Im}^n + \mathrm{Im} \longrightarrow {}^1\mathrm{Im}^0 + \mathrm{Im} \tag{2}$$

$$^1\mathrm{Im}^0 \longrightarrow {}^3\mathrm{Im} \tag{3}$$

$$^1\mathrm{Im}^0 \longrightarrow \mathrm{Im} \tag{4}$$

$$^3\mathrm{Im} \longrightarrow \mathrm{CF_3CN} + \mathrm{CF_3} + \mathrm{H} \tag{5}$$

$$^3\mathrm{Im} \longrightarrow \mathrm{Im} \tag{6}$$

$$\mathrm{CF_3} + \mathrm{Im} \longrightarrow \mathrm{CF_3H} + \mathrm{R_1} \tag{7}$$

$$\mathrm{CF_3} + \mathrm{Im} \longrightarrow \mathrm{R_2} \tag{8}$$

$$\mathrm{H} + \mathrm{Im} \longrightarrow \mathrm{H_2} + \mathrm{R_1} \tag{9}$$

$$\mathrm{H} + \mathrm{Im} \longrightarrow \mathrm{R_3} \tag{10}$$

$$\mathrm{R}_n + \mathrm{Im} \longrightarrow \text{polymer} \tag{11}$$

Here $^1\mathrm{Im}^n$ refers to the nth vibrational level of the first excited singlet imine, and $^3\mathrm{Im}$ refers to an undefined vibrational level of the lowest triplet. Fluorescence and phosphorescence are of little importance and have been omitted, and our results would allow either k_4 or k_6 to be 0. We consider that our data strongly suggest two dissociative modes: one a molecular split from a singlet state, and the other a radical split from the triplet state.

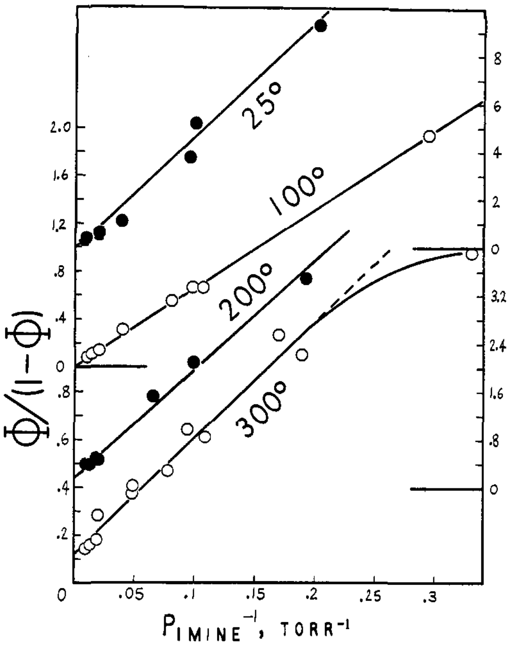

Figure 9. Plot of $\Phi(\mathrm{CF_3CN})/(1 - \Phi(\mathrm{CF_3CN}))$ *vs.* reciprocal of imine pressure. Ordinates: 25°, upper right ($\times 10^3$); 100°, upper left ($\times 10^2$); 200°, lower right ($\times 10^2$); 300°, lower left ($\times 10$).

Steady states in the transient species lead to

$$\Phi(\mathrm{CF_3CN}) = (k_1 + k[\mathrm{Im}])/(k_1 + k_2[\mathrm{Im}]) \tag{12}$$

where $k = k_2k_3k_5/(k_3 + k_4)(k_5 + k_6)$. We can obtain several rate constant ratios from eq 12. The slopes at the origin of the Φ^{-1} *vs.* [Im] plots give k_2/k_1. The slopes of the $\Phi/(1 - \Phi)$ *vs.* $[\mathrm{Im}]^{-1}$ plots give $k_1(k_2 - k)$ and estimates of Φ^{∞} values in Figures 2–5 give k/k_2. The ratios obtained are summarized in Table II. The product of the first two rows gives $k_2/(k_2 - k)$ and since this is near unity in each case it is evident that $k_2 \gg k$, as confirmed by the third row. At 25° the value of k_2/k_1 is 6.4×10^5 l. mol^{-1} and this may be compared with Bowers and Porter's[11] value of 8×10^2 for hexafluoroacetone at 265 nm. The large difference is due to the much greater deactivation that occurs with the imine. For example at 25° and 10 Torr Φ equals 0.8 for hexafluoroacetone but only 5×10^{-3} for the imine.

An Arrhenius plot of k_1/k_2 shows some curvature at the lower temperatures because the excited species concerned are not fully equilibrated.[11] The high temperature slope gives $E_1 - E_2 = 3.5$ kcal mol^{-1} which represents the lower limit of the critical energy for the decomposition of the vibrationally excited singlet reached when 254-nm radiation is absorbed.[11a]

The effect of oxygen in increasing Φ is most interesting (Figure 7). If we postulate that oxygen reacts with the vibration-excited singlet (where $\mathrm{Im}^* = {}^1\mathrm{Im}^n$) then at

$$\mathrm{Im}^* + \mathrm{O_2} \longrightarrow \mathrm{CF_3CN} + \mathrm{CF_3OOH} \tag{13}$$

sufficiently high $[\mathrm{O_2}]$, $\Phi(\mathrm{CF_3CN})$ tends to unity. This is not observed, which suggests that either a small fraction of the Im–$\mathrm{O_2}$ complexes results in $\mathrm{CF_3CN}$ formation or else $\mathrm{O_2}$ does not react with singlet imine but with the triplet. This is consistent with work on the photooxidation of hexafluoroacetone[12] and we therefore make the alternative postulate that $\mathrm{Im}^* = {}^3\mathrm{Im}$ in reaction 13. This leads to

$$\lim_{\mathrm{O_2} \to \infty} \Phi(\mathrm{CF_3CN}) = \frac{k_1/k_2 + k_3[\mathrm{Im}]/(k_3 + k_4)}{k_1/k_2 + [\mathrm{Im}]} \tag{14}$$

which is clearly less than unity. Substitution for k_1/k_2 from Table II, and taking the limiting values of $\Phi(\mathrm{CF_3CN})$ from Figure 7, gives $k_3/(k_3 + k_4) = 0.0081$ at 25° and 0.012 at 200°. Then $k(k_3 + k_4)/k_2k_3 = k_5/(k_5 + k_6) = 0.025$ at 25° and 0.25 at 200°.

The fate of the $\mathrm{CF_3OOH}$ in reaction 13 is presumably to give $\mathrm{CF_2O}$ and eventually $\mathrm{CO_2}$ as suggested by Heicklen.[12]

The great effect of added ethylene is shown in Figure 8. Our results are too scattered for much quantitative speculation but if ethylene rapidly deactivates $^1\mathrm{Im}^n$ to $^1\mathrm{Im}^0$ the limiting quantum yield will tend to k/k_2. That this is the case may be seen by comparing the limiting value of $\Phi(\mathrm{CF_3CN})$ in Figure 8 with the same limiting value in Figure 4. The runs with added $n\text{-}\mathrm{C_6F_{14}}$ are also plotted in Figure 4 and it is clear that $n\text{-}\mathrm{C_6F_{14}}$ deactivates in a similar manner to that of imine.

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(11) P. G. Bowers and G. B. Porter, *J. Phys. Chem.*, 70, 1622 (1966).

(11a) Note Added in Proof. An Arrhenius plot of k/k_2 gives a slope corresponding to ~6 kcal mol^{-1}. Assuming that k_3, k_4, and k_6 are independent of temperature, this value equals E_5, the activation energy for decomposition of the triplet state.

(12) J. Heicklen, *Advan. Photochem.*, 7, 57 (1969).

Secondary Processes. Reactions 0–11 lead to the following expressions for the quantum yields of CF_3H and H_2.

$$\Phi(CF_3H) = [k_1 + kk_7[Im]/(k_7 + k_8)]/(k_1 + k_2[Im]) \quad (15)$$

$$\Phi(H_2) = kk_9[Im]/(k_9 + k_{10})(k_1 + k_2[Im]) \quad (16)$$

That these expressions are of the correct form is apparent by taking the limiting values of [Im]. Then $\Phi^0(CF_3H) = 1$, $\Phi^\infty(CF_3H) = kk_7/k_2(k_7 + k_8)$, $\Phi^0(H_2) = 0$, and $\Phi^\infty(H_2) = kk_9/k_2(k_9 + k_{10})$. These limiting values predict that as [Im] increases, (CF_3H) will decrease in a parallel fashion to $\Phi(CF_3CN)$ but with a smaller limiting value. $\Phi(H_2)$ on the other hand will increase to its limiting value.

The limiting values of $\Phi(H_2)$ and $\Phi(CF_3H)$ can be estimated from Figures 2–5 and combined with k/k_2 to give approximate addition/abstraction ratios. We obtain $k_8/k_7 \simeq 70$, 50, and 20 at 100, 200, and 300°, respectively. These values may be compared with more accurate data recently obtained by Pritchard, *et al.*,[13] who photolyzed hexafluoroacetone in the presence of the imine. Their data yield $k_8/k_7 = 73$, 61, and 55 at the above temperatures and the agreement is most satisfactory. The rapid addition of CF_3 to imine results in the steady-state value of $[CF_3]$ being reduced to the point where no C_2F_6 could be detected in our products.

Similar treatment of $\Phi^\infty(H_2)$ gives $k_{10}/k_9 \simeq 0.2$, 0.4, 2, and 20 at 25, 100, 200, and 300°, respectively. Thus H atoms appear to abstract more readily than they add to the imine at the lower temperatures.

In conclusion, eq 12, 15, and 16 give a satisfactory account of the behavior of $\Phi(CF_3CN)$, $\Phi(CF_3H)$, and $\Phi(H_2)$ as [Im] changes. The independence of these functions of intensity shown in Figure 6 is also justified.

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(13) D. W. Follmer, S. Toby, and G. O. Pritchard, *J. Phys. Chem.*, **76**, 487 (1972).

A Comparison of Valence Shell and Core Ionization Potentials of Alkyl Iodides[1]

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Abstract: X-Ray photoelectron spectroscopy was used to study the relative ionization potentials of the iodine $3d_{5/2}$ level in a series of alkyl iodides and HI. Comparison of these data with the corresponding iodine $5p_{1/2}$ ionization potentials obtained from uv photoelectron spectroscopy establishes that the chemical shifts are probably due to variations in the electron distribution along the carbon–iodine bond and that the $5p_{1/2}$ level is destabilized about 0.14 eV by hyperconjugation.

It has recently been shown that the valence shell *n* lone pair ionization potentials of alkyl iodides, bromides, and chlorides correlate well with Taft's σ^* values (as used with the Hammett equation)[2] and even better with each other.[3] Similar correlations have been found between the iodide ionization potentials and those of a series of other alkyl-substituted groups.[4] We now report the $3d_{5/2}$ ionization potentials of a series of alkyl iodides. These results are compared with the valence shell ionization potentials to elucidate the probable cause of the chemical shifts and the magnitude of hyperconjugation in these compounds.

Experimental Section

The alkyl iodides are commercially available and were used without further purification.

The $3d_{5/2}$ binding energies were obtained using an X-ray photoelectron spectrometer which has previously been described in detail.[5] A mixture of the sample and the trifluoromethyl iodide used as the reference was introduced into the target chamber and irradiated with Mg Kα X-rays. The resulting spectra of the mixtures were well resolved, and the relative position of the sample peak was determined in each case by a least-squares fit of the two peaks with Gaussian functions. The observed spectra of the cases with greatest and least shifts relative to trifluoromethyl iodide (*tert*-butyl iodide and methyl iodide, respectively) are shown in Figure 1. In the case of hydrogen iodide, isopropyl iodide was used as a reference, but the tabulated shift is given relative to trifluoromethyl iodide.

The $3d_{5/2}$ peak was characterized in the usual way by its spin–orbit splitting behavior; it was chosen as a representative core level simply because it gives a relatively intense and easily characterized spectrum. The resulting $3d_{5/2}$ binding energies are summarized in Table I as chemical shifts relative to trifluoromethyl iodide. Table I also includes a summary of the iodine lone pair $5p_{1/2}$ ionization potentials from ref 3.

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(2) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(3) F. Brogli, J. A. Hashmall, and E. Heilbronner, *Helv. Chim. Acta*, in press.

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(5) C. S. Fadley, S. B. M. Hagstrom, M. D. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48** (8), 3779 (1968).