Infrared Laser Induced Bromination and Chlorination of Chlorodifluoromethane[1]

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Single-pulse irradiation of $CHClF_2$–Br_2 gas mixtures at 1088 cm^{-1} and doses of 0.25–0.6 J/cm^2 produced up to 64% reaction. With excess Br_2, the product was mainly $CBrClF_2$, with CBr_2F_2 and $(CBrF_2)_2$ as byproducts. Use of $CDClF_2$ in place of $CHClF_2$ reduced the relative yield of $CBrClF_2$. Kinetic absorption spectroscopy showed that reaction products appear after an induction period of ~1 μs and that the disappearance of Br_2 becomes detectable after ~10 μs. The dominant process leading to $CBrClF_2$ is inferred to be the chain reaction $Br + HCClF_2 \rightarrow HBr + CClF_2$, $CClF_2 + Br_2 \rightarrow CBrClF_2 + Br$. Similar single-pulse irradiation of $CHClF_2$–Cl_2 gas mixtures at 1088 cm^{-1} produces $CCl_2F_2 + HCl$ in ~98% yield; $CClF_3$ and CCl_3F are minor products.

Bromochlorodifluoromethane, a useful fire retardant, can be synthesized on an industrial scale by high-temperature gas-phase bromination of $CHClF_2$,[2] in some cases with a solid metal oxide catalyst.[3] We report the laboratory synthesis of $CBrClF_2$ by pulsed IR laser irradiation of $CHClF_2$ at 1088 cm^{-1} in the presence of bromine (1088 cm^{-1} is in the region of the antisymmetric CF_2 stretching band). The analogous IR laser induced chlorination of $CHClF_2$ was studied as well.

The use of a pulsed IR laser for inducing high-temperature reactions offers the convenience that temperatures well over 1000 K can be reached, yet the heating and subsequent cooling of the gas take place so quickly that room-temperature IR gas cells may be used.

In the absence of halogen, $CHClF_2$ irradiated at 1088 cm^{-1} under similar conditions decomposes to $HCl + C_2F_4$, according to the mechanism shown in (1) and (2).[4] In the

$$CHClF_2 \rightleftarrows CF_2 + HCl \tag{1}$$

$$2CF_2 \rightarrow C_2F_4 \tag{2}$$

presence of Cl_2 or Br_2 the formation of C_2F_4 becomes insignificant.[5a] With Cl_2 there results CCl_2F_2 in nearly quantitative yield. With Br_2 there results $CBrClF_2$ as the major organic product, as well as substantial amounts of CBr_2F_2 and $CBrF_2CBrF_2$. Results of single-flash irradiations are listed in Table I, where S (substrate) denotes $CHClF_2$, $[S]_0$ and $[Br_2]_0$ denote partial pressures before irradiation, $-\Delta S$ is the decrease in S in one flash, E_{abs} is the energy absorbed per mole of $CHClF_2$ in the portion of gas (about 75% of the cell volume) actually exposed to the IR laser beam, and θ_M is the maximum temperature that would be reached in the irradiated volume if E_{abs} adiabatically became random thermal energy.

As shown in Table I, the fractional yield of $CBrClF_2$ depends both on E_{abs} and on the mole ratio of $[Br_2]/[S]$. Fractional yields in excess of 70% are readily obtained.

We were especially interested in the time evolution of the reaction products, which was examined by kinetic absorption spectroscopy. For $CHClF_2$, excited similarly at 1088 cm^{-1} in the absence of halogen, decomposition according to (1) is preceded by an induction period of 0.5–4 μs, depending on E_{abs} and (to a lesser extent) on pressure.[5b] This induction period, it is believed, reflects the finite amount of time required for the absorbed energy to flow into the reaction coordinate. It is conceivable that when halogen is added, the primary reaction step (and hence the reaction coordinate) might change, and the induction period might disappear.

In fact the induction period does not disappear. For example, Figure 1 shows tracings of optical transmission at 249 nm vs. time after IR laser excitation for two typical experiments under conditions that are described in the caption. (Note the difference in time scales and vertical expansion.) The change in transmission is preceded in both cases by an induction period of ~1 μs. Of the species that are, or might be, present in the laser-excited gas, the following absorb considerably at 249 nm: CF_2, ϵ 1000 ± 200 M^{-1} cm^{-1};[5b] $CBrF_2$ radicals, ϵ ~700;[9] CBr_2F_2, ϵ ~430.[7–9] Br_2 (ϵ ~2),[11,12] Br (ϵ 0), $(CBrF_2)_2$ (ϵ 72), and $CHClF_2$ do not,[5b] and $CBrClF_2$ is unlikely to,[9] absorb significantly at 249 nm. Molar extinction coefficients ϵ (base 10, M^{-1} cm^{-1}) are stated for the laser-excited gas.

A time lag or induction period also appears when optical transmission is measured at 436 nm, where Br_2 is the sole absorbing species (Figure 2, lower trace; Figure 3). These results are informative and deserve further discussion.

It is known, from both theory and experiment,[10,11] that the molar extinction coefficient of Br_2 at 436 nm decreases with increasing temperature. The "temperature" governing this phenomenon is the Br_2 vibrational temperature. The manner in which this phenomenon affects optical transmission after an infrared laser flash in the absence of chemical reaction is shown in the upper trace of Figure 2. In this experiment, a gaseous SiF_4–Br_2 mixture is irradiated at 1025 cm^{-1}, where SiF_4 absorbs strongly, so that $\theta_M = 1370 \pm 70$ K. The Br_2 vibrational temperature rises with a significant half-time. Optical transmission at 436 nm reaches a plateau after about 3 μs and indicates a Br_2 vibrational temperature of 1260 ± 60 K, based on available ϵ vs. T data.[11] The discrepancy between θ_M and the plateau temperature of Br_2 is not statistically significant.

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[1] Work supported by a grant from the National Science Foundation.

[2] (a) Massone, J. British Patent 1127394; *Chem. Abstr.* **1969**, *70*, 3253. (b) Firestone Tire and Rubber Co., U.S. Patent 2731505, 1952. (c) Wang, Y. L.; Kuo, H. C.; Wang, S. S.; Lin, Y. T. *Hua Hsueh Hsueh Pao* **1965**, *31*, 531–5; *Chem. Abstr.* **1966**, 64, 11835*d*.

[3] (a) Dow Chemical Co., U.S. Patent 2871274, 1955. (b) Farbwerke Hoechst, A. G. Belgian Patent 631933 (1963); *Chem. Abstr.* **1964**, *60*, 14385*a*.

[4] Grunwald, E.; Olszyna, K. J.; Dever, D. F.; Knishkowy, B. *J. Am. Chem. Soc.* **1977**, *99*, 6521–7.

[5] (a) The only experiment in which some C_2F_4 was detected involved irradiation of 20.5 torr of $CHClF_2$ and 16 torr of Br_2 with a high IR dose so that 45% of the $CHClF_2$ reacted in one flash. (b) Lonzetta, C. M.; Grunwald, E., submitted for publication in *J. Phys. Chem.*

[6] Dalby, F. W. *J. Chem. Phys.* **1964**, *41*, 2297–2303. Modica, A. P. *J. Phys. Chem.* **1968**, *72*, 4594–8.

[7] Davidson, N. A. *J. Am. Chem. Soc.* **1951**, *73*, 467–8.

[8] Doucet, J.; Gilbert, R.; Sauvageau, P.; Sandorfy, C. *J. Chem. Phys.* **1975**, *62*, 366–9. Doucet, J.; Sauvageau, P.; Sandorfy, C. *Ibid.* **1973**, *58*, 3708–16.

[9] For $CBrF_2$, the estimate of ϵ is derived from kinetic spectroscopy of the decomposition of CBr_2F_2. For IR laser excited CBr_2F_2, ϵ was measured by Garcia and Grunwald. Values of λ_{max} for the first UV absorption band are, at 300 K, as follows: $CHClF_2$, 151 nm; $CBrClF_2$, 205 nm; $CBrF_2CBrF_2$, <204 nm; CBr_2F_2, 229 nm.

[10] Sulzer, P.; Wieland, K. *Helv. Phys. Acta* **1952**, *25*, 653–76.

[11] Passchier, A. A.; Christian, J. D.; Gregory, N. W. *J. Phys. Chem.* **1967**, *71*, 937–42.

[12] Wen, W. Y.; Noyes, R. M. *J. Phys. Chem.* **1972**, *76*, 1017–8.

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Table I. Products from IR Pulse Irradiation of $CHClF_2 + Br_2$ at 1088 cm^{-1}

no.	$[S]_0$, torr	$[Br_2]_0$, torr	E_{abs},[a] kJ/mol	θ_M, K	$-\Delta[S]^b/[S]_0$	$[CBrClF_2]^c/[S]_0$	$[CBr_2F_2]^c/[S]_0$	$2[(CBrF_2)_2]^c/[S]_0$	fraction[d] of $CBrClF_2$
1	14.4	4.6	68	1127	0.072	0.050	0.021	0.014	0.62
2	15.4	3.6			0.208	0.090	0.023	0.078	0.46
3	15.0	4.0	129	1760	0.487[e]	0.138	0.051	0.181	0.34
4	14	21			0.17	0.157	0.036	0.013	0.83
5	16.3	18.7	100	1210	0.307	0.221	0.065	0.033	0.70
6	14.8	20.4			0.382	0.250	0.095	0.041	0.65
7	17.9	36.1			0.166	0.134	0.020	0.009	0.82
8	15.5	38.5	108	1054	0.310	0.215	0.061	0.009	0.73
9	15.2	38.8	168	1415	0.638	0.408	0.149	0.071	0.65
	$CDClF_2$ +	Br_2							
10	11.2	40			0.124	0.107	0.029	0.000	0.81

[a] kJ/mol of $CHClF_2$. [b] Measured by IR spectrophotometry, with standard error being the greater of 10% or 0.02. [c] Measured by GLC, with standard error being the greater of 5% or 0.002. [d] Average of $[CBrClF_2]/(-\Delta[S])$ and $[CBrClF_2]/([CBrClF_2] + [CBr_2F_2] + 2[(CBrF_2)_2])$. Formation of C_2F_4 is not detectable in the experiments. [e] In this experiment the mass balance, unaccountably, is only 76%. We doubt that this is significant and suspect inane error.

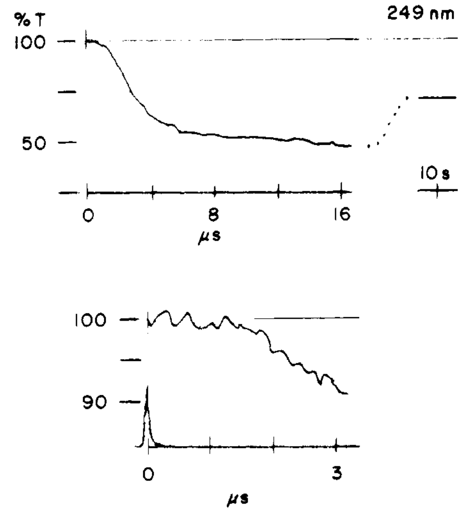

Figure 1. Optical transmission at 249 nm following excitation by an infrared laser pulse at 1088 cm^{-1}. Upper trace, 15.0 torr of $CHClF_2$ + 4.0 torr of Br_2, E_{abs} = 129 kJ/mol of $CHClF_2$, θ_M = 1760 K. For reaction products see Table I, line 3. Lower trace, 16.2 torr of $CHClF_2$ + 38 torr of Br_2, E_{abs} = 170 kJ/mol of $CHClF_2$, θ_M = 1400 K. Reaction products are essentially those shown in Table I, line 9. IR pulse power profile traced on bottom.

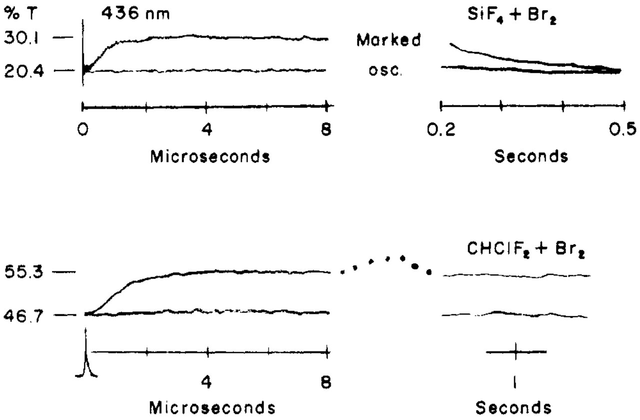

Figure 2. Optical transmission at 436 nm following excitation by an infrared laser pulse. Upper trace, 12 torr of SiF_4 + 40 torr of Br_2, E_{abs} = 197 kJ/mol of SiF_4 at 1025 cm^{-1}, θ_M = 1370 K. The return to the original transmission after 0.2–0.5 s was measured in a separate experiment. Lower trace, 16.3 torr of $CHClF_2$ + 18.7 torr of Br_2, E_{abs} ~100 kJ/mol of $CHClF_2$ at 1088 cm^{-1}, θ_M = 1210 K. Reaction products are in Table I, line 5.

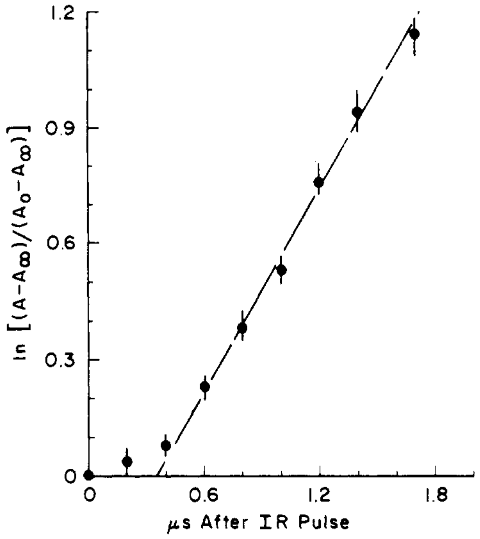

Figure 3. First-order kinetics plot for bromine absorbance vs. time during the first 2 μs after the laser flash: 16.3 torr of $CHClF_2$ + 18.7 torr of Br_2, E_{abs} ~100 kJ/mol of $CHClF_2$. The plot is based on transmission at 436 nm, as shown in the lower trace of Figure 2. A_∞ = 0.244, based on average transmission during the period 4–8 μs. A_0 = 0.331. A = absorbance at time t.

Subsequent cooling of the SiF_4–Br_2 gas back to room temperature is accompanied by oscillations of pressure and temperature, leading to marked oscillations in optical transmission. These subside eventually, and the upper right trace of Figure 2 shows the return to the initial value. This laser-induced cycle of transmission changes can be repeated numerous times. According to known rate constants,[13] dissociation of Br_2 to Br atoms is unimportant in 8 μs.

Returning to the system $CHClF_2$–Br_2, we see in the lower trace of Figure 2 the optical transmission at 436 nm vs. time when a $CHClF_2$–Br_2 mixture is irradiated at 1088 cm^{-1} so that θ_M = 1210 ± 70 K. In this case, optical transmission reaches a plateau after about 6 μs and indicates a Br_2 vibrational temperature of 1160 ± 50 K at the plateau, in reasonable agreement with θ_M. These data are consistent with the hypothesis that disappearance of Br_2 by chemical reaction is insignificant (<2%) during the first 6 μs and that the presence of Br_2 does not accelerate the normal laser-induced disappearance of $CHClF_2$ according to (1) (~2% in 6 μs at 1200 K).[5b]

Disappearance of Br_2 *does* become evident at later times. Our kinetic spectroscopy records include photographs of two experiments taken on 100-μs and 1-ms time scales

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(13) Palmer, H. B.; Hornig, D. F. *J. Chem. Phys.* **1957**, *26*, 98–105.

which show it unmistakably. After reaching a plateau in a few microseconds, optical transmission at 436 nm departs from the plateau between 10 and 100 μs and increases slowly, except for oscillations owing to gas dynamic effects. Eventually, at unknown times after 1 ms, optical transmission decreases again as the gas cools down to room temperature. The final transmission is higher than that before the IR pulse, the inferred decrease of Br_2 being consistent with the amount of bromination products. The results indicate that bromination of $CHClF_2$ in these experiments takes place relatively slowly, on an 0.1–1-ms time scale.

The time lag preceding the rise in the Br_2 vibrational temperature (Figure 2, lower trace) is brought out more clearly by the first-order kinetic plot constructed from these data in Figure 3. A reasonable interpretation which can account both for the initial lag and the subsequent, practically first-order kinetics is as follows. The energy absorbed from the laser beam, which is initially vibrational energy of $CHClF_2$, is released to translational and rotational modes during the lag period and raises the translational/rotational (T/R) temperature of the gas. The vibrational temperature of Br_2 is raised subsequently by T–V energy transfer. Because of the relatively small vibrational heat capacity of Br_2, the T/R temperature drops only slightly during this process, and T–V transfer to Br_2 proceeds with approximately pseudo-first-order kinetics, in agreement with Figure 3. According to this interpretation, the induction period preceding the $CHClF_2$ decomposition (e.g., Figure 1) could also be closely related to the rise in the T/R temperature of the gas.

Under the high-energy conditions of the present experiments the irradiated gas emits an orange glow, probably due to the return of excited $^3Br_2$ molecules to the singlet ground state.[14]

Chlorination of $CHClF_2$ seems to follow a similar kinetic pattern. Figure 4 traces optical transmission vs. time after an IR pulse at 334 nm, where Cl_2 absorbs. The rapid decrease in absorbance during the first 2 μs is mostly due to the rise in the Cl_2 vibrational temperature.[10] This is followed by a slower decrease, which is reasonably ascribed to disappearance of Cl_2 by reaction with $CHClF_2$ or with CF_2, produced by reaction 1.

Reaction Mechanism. Bromination. Most of the present work concerns the IR laser induced *bromination* of $CHClF_2$. It seems clear from the results, Figures 1–3, for example, that bromination does not become significant immediately after the laser pulse. Disappearance of Br_2, after the initial temperature rise, is not obvious in Figure 2 even after 8 μs. A reasonable explanation is that $CBrClF_2$ results mostly from the chain reaction in eq 3 and 4 and

$$Br + HCClF_2 \rightarrow HBr + CClF_2 \qquad (3)$$

$$Br_2 + CClF_2 \rightarrow CBrClF_2 + Br \qquad (4)$$

that an initial lag is needed to build up the Br atom concentration. For (3), $\Delta H^\circ \approx 63$ kJ and $E_{act} \approx 74$ kJ.[15,16] For (4), $\Delta H^\circ \approx -71$ kJ and E_{act} is probably less than 10 kJ.[17] Because of the moderately high activation energy for (3), this reaction path is sensitive to temperature and becomes quenched relatively early as the gas cools to room temperature. We estimate, by analogy to cooling curves obtained by D. Garcia in this laboratory, that the effective reaction time is about 5 ms, within a factor of 2.

For the typical experiment in the lower trace of Figure 2, adopting $T = 1100$ K, the Br atom concentration is 5×10^{-5} M when equilibrium with Br_2 exists.[18] Under those conditions, to produce the observed yield of $CBrClF_2$ would require about 1 ms,[16] which is an acceptable length of time.

On the other hand, it is doubtful whether the *direct* dissociation of Br_2 after the laser-induced *T*-jump is fast enough. Experimental rate constants for Br_2 dissociation in a bromine-rich gas phase show considerable variation,[12] and half-times for approach to equilibrium at 1100 K and 0.001 M Br_2 are between 3 and 20 ms. However, the data permit the interpretation that Br formation is accelerated by the mechanism

$$CHClF_2 \rightarrow CF_2 + HCl \qquad (1)$$

$$CF_2 + Br_2 \rightarrow [CBr_2F_2]^* \rightarrow CBrF_2 + Br \qquad (5a)$$

$$\xrightarrow{+M} CBr_2F_2 \qquad (5b)$$

In Figure 1, where θ_M is 1760 and 1400 K, respectively, the marked decrease in optical transmission at 248 nm could be due to the presence of either CF_2 or of varying mixtures of CF_2 with $CBrF_2$ and CBr_2F_2, since the molar extinction coefficients of these species are of similar magnitudes. (See previous section.) In the lower trace of Figure 2, where θ_M is only 1200 K, similar reactions may be occurring, but the decrease in Br_2 at this temperature is expected to be less than 2% on the time scale shown, which is too small to be detected.

At gas pressures of 30–60 torr, one would expect (5a) to be quite significant in competition with (5b). The vibrational energy of $[CBr_2F_2]^*$ resulting from $CF_2 + Br_2$ is ~280 kJ/mol at 1100 K, while the C–Br bond dissociation energy of structural analogues of CBr_2F_2 is 265–287 kJ/mol.[19,20] Reactions 5 are much faster than (2), as shown by the practical absence of C_2F_4 from the reaction products. The presence of $(CBrF_2)_2$ among the reaction products indicates that $CBrF_2$ radicals were present at an earlier stage. Bromine atoms and CBr_2F_2 may also result from the reaction

$$CBrF_2 + Br_2 \rightarrow CBr_2F_2 + Br$$

Comparison of lines 7 and 10, Table I, shows that formation of $CBrClF_2$ is ~30% faster from $CHClF_2$ than from $CDClF_2$, under conditions where the fractional yields of $CBr_2F_2 + 2(CBrF_2)_2$ are equal. Although quantitative considerations are premature, a negative deuterium isotope effect is consistent with the proposed mechanism centered on (3) and (4).

Chlorination. Our studies of the IR laser induced chlorination of $CHClF_2$ are less detailed. However, it is probable that the reaction mechanism is similar. Under conditions similar to those of experiment 5 in Table I, the yield of CCl_2F_2 is nearly quantitative. Consistent with this, the activation energy for the analogue of (3), $Cl + HCClF_2 \rightarrow HCl + CClF_2$, is much lower; we estimate 25 kJ/mol.[17] As in the case of bromination (eq 3 and 4) the chain-

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(14) Browne, R. J.; Ogryzlo, E. A. *J. Chem. Phys.* **1970**, *52*, 5774–80.

(15) In addition to values in ref 18, the following estimates of ΔH°_f were used: $CClF_2$, −64 kcal (−268 kJ); CBr_2F_2, −99 kcal (−414 kJ); $CBrF_2$, −33 kcal (−138 kJ).

(16) For Br + HCF_3, log A = 9.99, E_{act} = 93 kJ; for Br + $HCCl_2F$, log A = 10.02, E_{act} = 56 kJ. For Br + $HCClF_2$, we estimate log A = 10.01, E_{act} = 74 kJ. The units of A are $M^{-1}\,s^{-1}$. Based on data in "Rate Constants of Gas Phase Reactions", Kondratiev, N. V., Ed. (Publication COM 72-10014, National Technical Information Service, Springfield, VA 22151), January 1972.

(17) For typical activation energies see: Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: England, 1974; Chapters 7 and 8.

(18) "JANAF Thermochemical Tables", 2nd ed. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, No. C13.14:37.

(19) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions". *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, No. C 13.48:21.

(20) Pickard, J. M.; Rodgers, A. S. *Int. J. Chem. Kinet.* **1977**, *9*, 759–67.

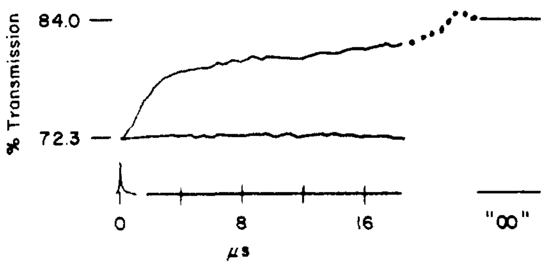

Figure 4. Optical transmission at 334 nm following excitation of $CHClF_2$ by a 1088-cm^{-1} IR pulse: 15.3 torr of $CHClF_2$ + 25.7 torr of Cl_2, E_{abs} ~95 kJ/mol of $CHClF_2$. The initial gas mixture contains a trace of HCl. Better than 95% of the $CHClF_2$ is converted to CCl_2F_2. Total exposure of the reaction mixture to the UV monitoring light is 1.1 min. Control experiments show that UV-catalyzed photochemical reaction is practically negligible under the stated conditions. The solid lines connect experimental points; the dotted line is a presumed interpolation.

carrying halomethyl radical is $CClF_2$. As in the case of bromination, the yields of $(CClF_2)_2$—the dimer of the chain-carrying radical—and of C_2F_4 are too small to be detected. Gas chromatography does detect traces (~1%) of $CClF_3$ and CCl_3F among the reaction products.

Experimental Section

Materials. $CHClF_2$ and chlorine (high purity) were obtained from Matheson Gas Products. CBr_2F_2 and $CBrClF_2$ were obtained from PCR, Inc. Liquid bromine was from Fisher Scientific Co.

$CDClF_2$ was synthesized by photochemical reaction of chlorine gas with CD_2F_2 (Merck, Canada) and isolated by preparative GLC in chemical purity of better than 99.9% and isotopic purity (with respect to $CHClF_2$) of ~99.9%. Inasmuch as product yields were considerably better than by a previously reported procedure,[21] a typical synthesis will be reported.

Degassed oxygen-free 194-torr CD_2F_2 and 290-torr Cl_2 are introduced into a vacuum-tight 2.6-cm long stainless steel reaction cell equipped with front-and-back KCl windows for IR monitoring and transverse quartz windows for UV-Vis irradiation. A $^3/_{16}$-in. diameter collimated beam from a 200-W xenon-mercury arc is allowed to pass radially through the gas, and progress of the photochemical chlorination is monitored by IR spectrophotometry. After 20 h, >93% of the initial CD_2F_2 is converted to 90 ± 3% $CDClF_2$ and 7 ± 2% CCl_2F_2. (If oxygen is not completely removed, there will also be some CF_2O.) The reaction cell is then attached to the inlet port of a preparative gas-liquid chromatograph and the components are separated on a $^1/_4$-in. diameter, 2-m long stainless steel column at 125 °C, packed with 80–100 mesh Poropak Q. The $CDClF_2$ fraction, which is well resolved from the others, is collected at liquid N_2 temperature in a special apparatus consisting of a glass U-tube equipped with stainless steel vacuum valves and fittings to permit subsequent degassing and transfer to other apparatus. Repeated injections, using a Varian six-port valve, into the GLC apparatus are needed to collect >90% of the reaction product.

Analytical Procedures. Reactant mixtures were prepared on a vacuum line. First, the halogen gas was introduced into the reaction cell on a grease-free stainless steel line, pressure was measured with a Texas Instruments Model 140A fused-quartz pressure gauge, and then the other component was added on a glass line. Total pressure was measured by either a Hg or oil manometer. Partial pressure of the other component was obtained by IR spectrometry, and partial pressure of Br_2 or Cl_2 was then obtained from the total pressure by difference and checked by UV-Vis spectrometry.

The stainless steel reaction cell with flat, polished KCl infrared windows and sapphire UV-Vis windows (transverse to the KCl windows) has been described elsewhere.[5b] After introduction of the reactant gases, an infrared and UV-Vis spectrum was taken, an infrared laser pulse was applied, and the products were analyzed by taking another infrared and UV-Vis spectrum without removing the gases from the reaction cell. The cell was then attached to the gas inlet port of a GLC apparatus,[22] and the components were separated on a 2 m × $^1/_8$-in. Poropak Q column with nitrogen carrier and determined with a flame-ionization detector.[23] Column temperatures were variously adjusted to 88, 125, and 160 °C. Except for $(CBrF_2)_2$, the flame-ionization detector signal was calibrated as a function of component partial pressure by careful experiments involving authentic samples. For $(CBrF_2)_2$, data were obtained from laser irradiation of CBr_2F_2. Relative retention times at 125 °C: $HCClF_2$, 110; $CBrClF_2$, 330; CBr_2F_2, 760; $(CBrF_2)_2$, 1660 s. Relative flame-ionization response factors (signal area per torr): $HCClF_2$, 1.66; $CBrClF_2$, 2.32; CBr_2F_2, 2.69; $(CBrF_2)_2$, 11.5. The response factors were independent of pressure in the experimental range. Molar extinction coefficients ($torr^{-1}$ cm^{-1}) for spectrometry: CBr_2F_2, 0.0236 at 1140 cm^{-1}, 0.0270 at 1080 cm^{-1}, 0.0261 at 1072 cm^{-1}, 0.0382 at 822 cm^{-1}, 0.0429 at 816 cm^{-1}; $(CBrF_2)_2$, 0.0187 at 1008 cm^{-1}, 0.0536 at 766 cm^{-1}; $CBrClF_2$, 0.00801 at 1155 cm^{-1}, 0.0159 at 1140 cm^{-1}, 0.0227 at 1090 cm^{-1}, 0.0226 at 1072 cm^{-1}, 0.0142 at 882 cm^{-1}, 0.0224 at 869 cm^{-1}, 0.0258 at 862 cm^{-1}, 0.0218 at 857 cm^{-1}.

Absorption from Pulsed IR Laser Beam. The relation of E_{abs} to infrared dose (D, expressed in J/cm^2) at 1088 cm^{-1} for $CHClF_2$ in the presence of Br_2 followed the equation E_{abs} (kJ/mol of $CHClF_2$)/D = 19.5 + $399P_{eff}/(P_{eff} + 22.06)$ where $P_{eff} = P_{CHClF_2} + 1.2P_{Br_2}$ and pressure is expressed in torr.[4] D varied in the range 0.2–0.6 J/cm^2.

IR Laser Kinetic Absorption Spectroscopy. The infrared laser was a tunable pulsed Lumonics Model 103 TEA CO_2 laser. The effective IR pulse duration was ~300 ns. Details concerning the optical bench layout and infrared dosimetry have been reported previously.[4,5b] The light source for kinetic absorption spectroscopy was a 200-W xenon-mercury arc. Instrumentation used for transverse monitoring was identical with that described.[5b] The instrumental response time in most experiments was 50 ns. The UV-Vis light was kept out of the reaction cell by means of a shutter which was opened about 5 s before the arrival of the IR pulse and closed about 1 min after the IR pulse.

Control Experiments. To test for possible UV photochemistry induced by the xenon-mercury arc used in kinetic absorption spectroscopy, we performed two kinds of control experiments: (1) The results of IR irradiation were compared with and without the xenon-mercury arc turned on, under otherwise practically identical conditions. There was no significant difference in the nature and absolute amounts of the reaction products, neither for $CHClF_2$ + Br_2 nor for $CHClF_2$ + Cl_2. (2) A mixture of 12.8 torr of $CHClF_2$ + 26.7 torr of Cl_2 was placed in the IR reaction cell and exposed to the beam from the xenon-mercury arc, in the arrangement used for kinetic spectroscopy, for 45 s. A total of 0.3 torr of CCl_2F_2 was produced. The gas was then exposed to a single IR laser pulse at 1088 cm^{-1}. The amount of CCl_2F_2 went up to 12.1 torr, which was practically the same amount as obtained in a separate "dark" reaction.

Conceivably, $CBrClF_2$ might be formed in the secondary reaction $CBr_2F_2 + HCl \rightarrow CBrClF_2 + HBr$, the initial laser-induced reaction being $CHClF_2 + Br_2 \rightarrow CBr_2F_2 + HCl$. Accordingly, several experiments were done, using equimolar mixtures of CBr_2F_2 and HCl. When such mixtures were allowed to stand at room temperature for 1–4 h, GLC analysis showed barely detectable peaks at the retention time of $CBrClF_2$ and $CHClF_2$. When such mixtures were irradiated (with or without UV exposure) with a laser pulse at 1088 cm^{-1}, where CBr_2F_2 absorbs strongly, the only reaction product detected by IR spectrometry was $(CBrF_2)_2$. GLC analysis also showed barely detectable peaks at the retention times of $CBrClF_2$, $CHClF_2$, and CCl_2F_2. We conclude that the formation of $CBrClF_2$ by this route is practically negligible in our experiments.

Registry No. $CClF_3$, 75-72-9; CCl_3F, 75-69-4; $CHClF_2$, 75-45-6; Cl_2, 7782-50-5; CBr_2F_2, 75-61-6; $CBrClF_2$, 353-59-3; $CDClF_2$, 1495-14-3; CD_2F_2, 594-24-1; $(CBrF_2)_2$, 124-73-2; CCl_2F_2, 75-71-8; HCl, 7647-01-0; Br_2, 7726-95-6; SiF_4, 7783-61-1.

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