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MEGAWATT INFRARED LASER CHEMISTRY. II. USE OF SiF_4 AS AN INERT SENSITIZER.[1]

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Infrared irradiation of gases with a tunable pulsed CO_2 laser at power levels of 0.1-10 MW/cm^2 can induce chemical reaction.[2-4] When the reactant to be activated has a strong absorption band in the laser's tunable range, direct excitation of the reactant is convenient and efficient.[5] When the reactant does not absorb or absorbs only weakly in the tunable range, it is necessary to add a sensitizer. Ideally this should be a substance which absorbs the infrared radiation strongly, and transfers a sufficient portion of the absorbed energy to the gaseous species to be reacted without itself decomposing or participating in the reaction sequence.

SF_6 has been used as a sensitizer in experiments involving relatively low-power continuous CO_2 lasers (1 kw/cm^2 or less).[6] However, in MW/cm^2 irradiation with a pulsed laser, we find that SF_6 is not inert. Specifically, when 50 torr of SF_6 is irradiated at 935 cm^{-1} in the presence of ~ 50 torr of H_2, D_2, $(CH_3)_2CO$, CH_3OH, or CH_3CN, reaction occurs, as indicated by the formation of light-yellow odorous precipitates and the emission of visible light, whose color ranges from bluish-green for SF_6 + H_2 or D_2 to pale violet for SF_6 + CH_3CN. Infrared analysis shows consumption of SF_6 and formation of HF.

On the other hand, we find that SiF_4 is an excellent sensitizer for inducing chemical reactions with tunable CO_2 lasers. It absorbs strongly and remains unreactive in the presence of a wide variety of substrates at infrared power levels of 0.1-2 MW/cm^2 and dose/flash levels of 0.03-0.5 j/cm^2.[7] The triply degenerate Si-F stretching mode (ν_3) of SiF_4, centered at 1032 cm^{-1},[8] has an exceptionally high Beer's law extinction coefficient of 0.12 torr^{-1} cm^{-1}. For best energy absorption, the laser frequency is tuned to 1025 cm^{-1}, which places the radiation into the P-branch of the absorption band.

At the infrared power and dose levels used in the present work, the absorption coefficient of SiF_4 deviates from Beer's law. In general, for a constant gas phase composition and SiF_4 pressure, the absorption coefficient decreases with increasing dose/flash; for a constant dose/flash, it increases with increasing pressure of either SiF_4 or added gas.

Typical relationships, for SiF_4 with or without added cyclopropane, are shown in Fig. 1. The ordinate expresses absorbed energy formally per mole of SiF_4; at 1025 cm^{-1}, 1 einstein = 12.3 kj/mole. The Figure also shows the "temperatures" that would be reached if the energy absorbed were converted adiabatically into random thermal energy, and the percent conversion of cyclopropane per flash. "Temperatures" can be controlled by varying component pressures at a given dose or by varying dose at constant pressure.

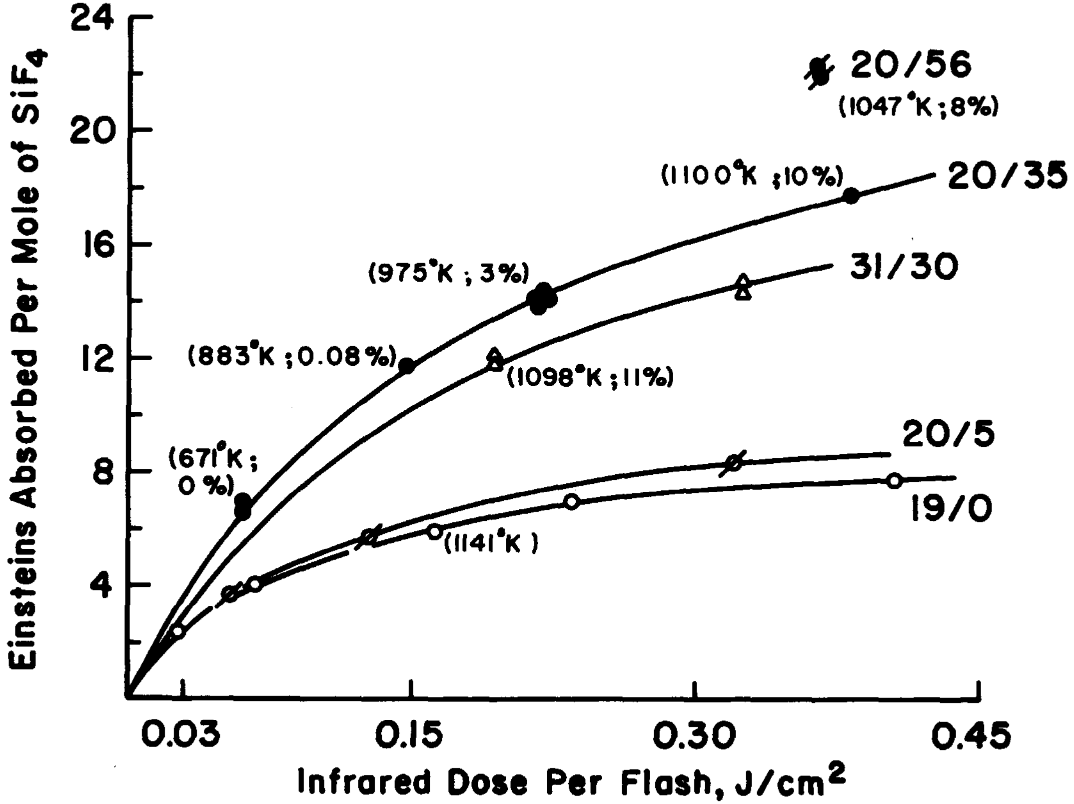
The chemical result of irradiation depends on component pressures and dose. At low dose no reaction occurs. As the dose is increased, cyclopropane becomes converted cleanly to propylene and, at still higher doses, one observes also the formation of methane, ethylene and acetylene. The latter appear to be decomposition products of propylene. There is no detectable decomposition of SiF_4.

SiF_4 was also irradiated in the presence of CH_3OH, $(CH_3)_2CO$, CH_3CHO, $(CH_3)_2O$, $HCClF_2$, and CF_2Cl_2. In each case it was possible to find conditions of dose/flash and pressure under which the added gas decomposed, while infrared analysis showed no change whatever in the SiF_4. According to Isenor and coworkers,[9] SiF_4 does decompose when irradiated at gigawatt/cm^2 infrared intensities, well above our experimental range.

The relative inertness of SiF_4, as compared with SF_6, under these conditions can be partially understood in terms of bond energies. The Si-F bond is exceptionally stable, not only in terms of absolute bond energy (Si-F = 610 kj/mole) but also when compared with other bonds to the silicon atom. For example, Si-H = 310 kj/mole. On the other hand, the S-F bond (300 kj/mole) is weak when compared with other sulfur bonds. For example, S-H = 370 kj/mole.[10]

The reactions sensitized by SiF_4 appear to be typical high-temperature decompositions. For example, irradiation of SiF_4 + $CHClF_2$ leads to the formation of C_2F_4 + HCl, which are also the known products of thermolysis.[11] Adopting the same reaction mechanism as for thermolysis,[11] the transient pressure of the reaction intermediate, $:CF_2$, under some of our conditions exceeds 1 torr. Irradiation of SiF_4 + $(CH_3)_2CO$ leads to $CH_2{=}C{=}O$ + CH_4 at moderate doses and to more complex mixtures, containing also C_2H_4, C_2H_2 and CO, at high doses. Because these products resemble those obtained in thermolysis, the primary decomposition steps could very well be identical: $CH_3COCH_3 \rightarrow CH_3\cdot + CH_3CO\cdot$.[12] These examples suggest that SiF_4 is relatively unreactive towards carbenes and free radicals even under conditions of high temperature.

Figure I. Plot of einsteins absorbed per mole of SiF_4 vs. infrared dose per flash (J/cm^{-1}) at 1025 cm^{-1} for mixtures of SiF_4 with cyclopropane. o 19 torr SiF_4 in absence of cyclopropane; ⌀ 20 torr SiF_4 with 5 torr cyclopropane; ● 20 torr SiF_4 with 35 torr cyclopropane; ⌀ 20 torr SiF_4 with 56 torr cyclopropane; △ 31 torr SiF_4 with 30 torr cyclopropane.



Where comparisons have been made, reaction products obtained from SiF_4 sensitized reaction are identical to those resulting from direct infrared excitation of the gaseous substrate in the absence of SiF_4. For example, direct excitation of $CHClF_2$ at 1088 cm^{-1} leads cleanly to $C_2F_4 + HCl$. Direct excitation of CCl_2F_2 at 921 cm^{-1} and SiF_4 sensitized reaction of CCl_2F_2 lead to the same products, which are consistent with a primary decomposition step of $CCl_2F_2 \rightarrow CClF_2\cdot + Cl\cdot$.[13] However, for the same amount of energy absorbed, direct excitation of CCl_2F_2 gives far better yields.[13]

The mechanism of intermolecular energy transfer between SiF_4 and added gas is currently under investigation.

References and Notes

1. (a) Work supported by a grant from the National Science Foundation; (b) see ref. 3a for Part I of this series.
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