Bull. Chem. Soc. Jpn., 68, 2817—2822(1995)

Photodissociation of CF_2Br_2 at 248 nm: A Time-Resolved Absorption Study

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(Received March 22, 1995)

Photodissociation of CF_2Br_2 at 248 nm has been studied in the gas phase using time-resolved optical absorption spectroscopy. A transient absorption spectrum in the range of 200—320 nm with $\lambda_{max} \approx 260$ nm is observed and has been assigned to the primary photodissociation product, the CF_2Br radical. The absorption cross section of this radical at 260 nm has been found to be $(1.05 \pm 0.2) \times 10^{-18}$ cm^2 molecule^{-1}. The rate constant for CF_2Br dimerization is evaluated to be $(3.0 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Laser fluence dependence in the secondary photodissociation of CF_2Br radical is discussed.

Understanding the atmospheric chemistry of halogen-containing organic compounds has assumed increased importance following recent observations of dramatic ozone loss.[1,2] Both bromine and chlorine were found to be engaged in catalytic destruction of ozone in similar cycles, with the former being more efficient. Bromine-containing compounds are released in large quantities in the atmosphere as a result of their use as fire retardants, fumigants, anaesthetics, etc. These compounds have long tropospheric life times.[3] The primary loss process for these bromomethanes is photolysis yielding either Br_2 or Br atoms.[4—6] The active bromine species Br and BrO undergo a catalytic cycle for ozone destruction.[7,8] Because of this, there has been a substantial interest in the photolysis studies of these compounds. In addition to this, the study of dissociation paths in simple molecules is of fundamental interest. The fragmentation of polyatomic molecules upon absorption of photons can proceed by a variety of dissociation pathways.[9,10] The study of underlying dissociation mechanisms has greatly contributed to our understanding of the dynamics of bond-breaking processes.

Photodissociation of CF_2Br_2 has received considerable attention because it has a possibility of multichannel photochemistry. In a number of studies, photolysis of this compound at 248 nm has been used as a source of generating and studying the reactions of CF_2 radicals with various other reactants. Following three channels have been reported in a number of studies on the IR[11—14] and UV photodissociation[15—23] of CF_2Br_2.

$$CF_2Br_2 \rightarrow CF_2Br + Br \quad \Delta H = 255 \text{ kJ mol}^{-1} \tag{1}$$

$$CF_2Br_2 \rightarrow CF_2 + Br_2 \quad \Delta H = 213 \text{ kJ mol}^{-1} \tag{2}$$

$$CF_2Br_2 \rightarrow CF_2 + 2Br \quad \Delta H = 435 \text{ kJ mol}^{-1} \tag{3}$$

The CF_2Br thus produced can undergo secondary photodissociation or unimolecularly decay to give CF_2 as shown below.

$$CF_2Br + h\nu \rightarrow CF_2 + Br \tag{4}$$

$$CF_2Br^* \rightarrow CF_2 + Br \tag{5}$$

In the UV photodissociation, an early study by Francis and Haszeldine[15] showed that CF_2Br_2 photolyzes readily in the presence of O_2 at wavelengths longer than 220 nm. In the 265 nm photolysis of CF_2Br_2, Walton[16] suggested that the primary process involves the formation of an excited species with a sufficiently long lifetime to be stabilized by collisions in competition with fragmentation. Molina and Molina[17] and recently Talukdar, Vaghjiani, and Ravishankara[18] measured the quantum yield to be unity for the photodissociation of CF_2Br_2 at 248 nm. Mann and Thrush[19] reported the CF_2 absorption spectrum in the flash photolysis of CF_2Br_2. Sam and Yardley[20] reported visible and near UV luminescence from CF_2 in the 248 nm photolysis. The fluorescence intensity was linear in radiation intensity in the fluence region 0.12—1.2 J cm^{-2}. Wampler, Tiee, Rice, and Oldenberg[21] also reported luminescence from CF_2, but observed a quadratic power dependence of the CF_2 fluorescence intensity for energy fluences between 3—9 J cm^{-2}. Using a crossed laser-molecular beam technique with a quadrupole mass spectrometer, Krajnovich, Zhang, Butler, and Lee[22] showed that the CF_2Br radical and Br atom are the primary products in the 248 nm photodissociation of CF_2Br_2. They also observed CF_2, which was attributed to the

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secondary photodissociation of some of the CF_2Br primary product. Gosnell, Taylor, and Lyman[23] used ultrafast time-resolved absorption spectroscopy to study the photodissociation of CF_2Br_2. They also detected the CF_2Br radical as the primary product. However, they concluded that the CF_2 radical is formed due to the unimolecular reaction of vibrationally hot CF_2Br intermediate species.

Although the primary channel and the quantum yield for the photodissociation of CF_2Br_2 at 248 nm have been reported, not much is known about the spectroscopy and kinetics of the primary product CF_2Br radical. Does it undergo unimolecular decomposition or absorb another photon to undergo secondary photodissociation or recombine to form $C_2F_4Br_2$? Out of these three channels, which one is the main decay route for CF_2Br and how is it affected by laser fluence? The origin and relative yield of CF_2 is also poorly understood.

In the UV region, CF_2Br_2 starts absorbing below 300 nm with a $\lambda_{max} \approx 229$ nm[16] and thus can be excited by a KrF laser. In our earlier work,[24] photodissociation of CF_2Br_2 was studied using a CO_2 laser as the excitation source. In this work, the results of 248 nm photodissociation of CF_2Br_2 in the gas phase have been reported. Further, the fate of CF_2Br has been discussed with reference to laser fluence.

Experimental

All the studies were done under static conditions by irradiating 10 Torr (1 Torr=133.322 Pa) of CF_2Br_2 using an excimer laser (Oxford lasers, 248 nm, 10 ns pulse width, 50 mJ/pulse) at a repetition rate of 1 Hz. The laser beam was focussed to an area of 0.2 cm^2. The time-resolved absorption studies were done in a stainless steel cell using crossed beam geometry for the laser and probe beams. The details have been described elsewhere.[25,26] The cw spectroscopic UV probe beam from a Xe lamp (150 W) with associated optics, monochromator (f=3.5), fast PMT, and a signal processing system (Gould Biomation 4500, 10 ns resolution) was part of a computer controlled laser kinetic spectrometer (Applied Photophysics, UK). A small portion of the laser light was allowed to fall on a photodiode whose output signal was used to trigger the digital oscilloscope. In some of the experiments, the monitoring Xe lamp was pulsed for better illumination in the UV region and the laser was triggered at a preset time when the lamp intensity reached a maximum and remained steady over a period of about 200 μs.

The dissociation yield measurements and product analyses were done either on an FT-IR spectrometer (Mattson, Cygnus 100) or by GC analysis using a carbowax column and a flame ionization detector with nitrogen as the carrier gas.[24] In a typical experiment, a 10 Torr sample was irradiated at a fluence of 0.25 $J\,cm^{-2}$ for 200 pulses and the contents of the cell were transferred to the injection port by multiple transfers. Under these irradiation conditions the total sample decomposed is typically about 6% of the initial pressure. CF_2Br_2 and C_2F_4 were calibrated using standard mixtures before analysis. CF_2Br_2 (Aldrich) was degassed by several freeze-pump-thaw cycles before use.

Results and Discussion

CF_2Br_2 (10 Torr) was irradiated with the KrF laser (50 mJ/pulse) under partially focussed conditions. Stable product analysis showed $C_2F_4Br_2$, C_2F_4, and Br_2 as the major products. From the FT-IR analysis, the yield of $C_2F_4Br_2$ accounts for 90% of the CF_2Br_2 dissociation. Gas chromatographic analysis showed the total yield of C_2F_4 to be 11% of the CF_2Br_2 dissociated. Since no other product is observed this gives 89% for $C_2F_4Br_2$, in agreement with the FT-IR data.

In the time-resolved UV absorption studies, a transient signal (Fig. 1) was observed. The rise time of the signal was found to be limited by the response time of the detection system (ca. 50 ns). The transient species absorbs in the range of 200—320 nm with a $\lambda_{max} \approx 260$ nm. The spectrum shown in Fig. 2 was taken at 2 μs delay with a wavelength resolution of 3 nm. Addition of 100 Torr of N_2 during the irradiation also did not cause any observable change in the spectrum, indicating that the transient spectrum is not due to any hot species.

In the photolysis of CF_2Br_2, two transient species that have been observed are CF_2Br and CF_2. Transient absorption of CF_2 is reported in the flash photolysis of this molecule[19] in the region 230—270 nm with λ_{max} around 250 nm. In these studies the spectrum lies in the region 200—320 nm and λ_{max} is shifted by about 10 nm. In addition the absorbance at 260 nm is about two times higher than that at 249 nm. This cannot be true if the transient is CF_2. To further differentiate between CF_2 and CF_2Br, the decay of the transient was investigated in the presence of O_2 and NO. The reaction

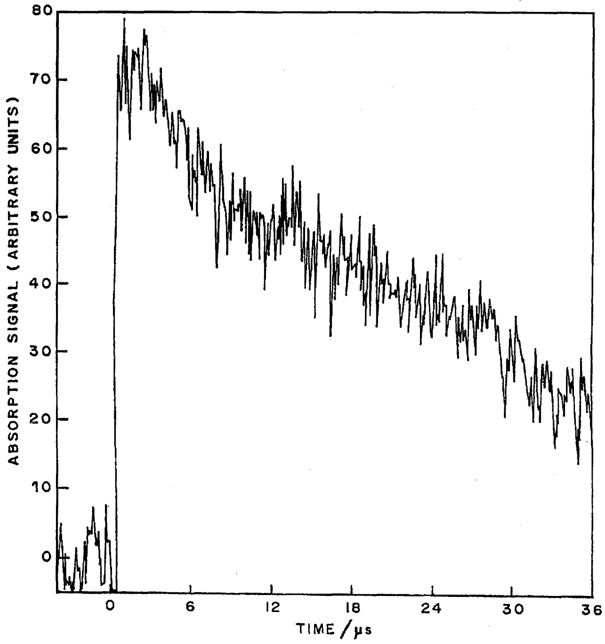

Fig. 1. Transient absorption signal of CF_2Br at 260 nm. (CF_2Br_2 10 Torr, laser fluence 0.25 $J\,cm^{-2}$).

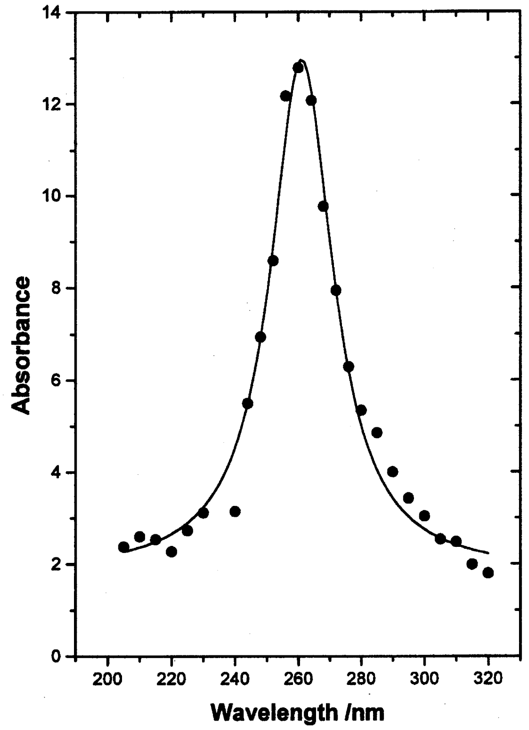

Fig. 2. Transient UV absorption spectrum of CF_2Br in 248 nm photolysis of CF_2Br_2 (pressure 10 Torr, wavelength resolution of 3 nm at 2 μs delay laser fluence 0.25 $J\,cm^{-2}$).

of CF_2 with O_2/NO is known to be slow.[27)] However, in these experiments, it was observed that the transient decays faster in presence of O_2/NO. All these results imply that the transient absorption is not due to CF_2 but from the other species generated in the photolysis. This is further supported by a faster recombination rate constant than that of CF_2 recombination[28)] (see Section 3). The major product after irradiation is $C_2F_4Br_2$, indicating that CF_2Br is the precursor, which dimerizes to give the observed product. Thus, we have assigned the observed spectrum to the CF_2Br radical.

1. Secondary Photodissociation vs. Unimolecular Decay of CF_2Br. The CF_2Br, formed as a result of the primary dissociation step, can either absorb a photon or can spontaneously dissociate. The former process requires that its absorption cross section at 248 nm should be large but for the latter process the internal energy should be sufficient to break the CF_2–Br bond. Krajnovich, Zhang, Butler, and Lee (Ref. 22, hereafter KZBL) have attributed the formation of CF_2 in 248 nm photolysis of CF_2Br_2 to the secondary photodissociation of CF_2Br on the basis of their smeared time-of-flight spectra of CF_2. Gosnell, Taylor, and Lyman (Ref. 23, hereafter GTL) in their ultrafast time-resolved absorption experiments observed an increase in the absorbance with increasing delay times after the laser pulse (FWHM 700 fs) was over. The species responsible for absorbance was identified as CF_2 and the increase in absorbance was attributed to the generation of CF_2 radicals from unimolecular decay of hot CF_2Br. The results of these two studies, though in general agreement, differ from each other regarding the origin of CF_2.

The kinetic scheme for the CF_2 yield coming as a result of secondary photodissociation of CF_2Br is given by

$$CF_2Br_2 \xrightarrow{k_1=\sigma_1 I} CF_2Br \xrightarrow{k_2=\sigma_2 I} CF_2 \tag{6}$$

The total fraction of CF_2 radicals produced due to secondary photodissociation is given by Eq. 7.[22,29)]

$$\frac{n_{CF_2}}{n_0} = 1 + \frac{\sigma p(-\sigma_2\phi) - \exp(-\sigma_1\phi)}{(\sigma_2)} \tag{7}$$

Here I is photon intensity in photons $cm^{-2}\,s^{-1}$ and ϕ is the time integrated photon flux. σ_1 and σ_2 are the absorption cross sections (in $cm^2\,molecule^{-1}$) of CF_2Br_2 and CF_2Br at 248 nm respectively, and n_0 is the no. density of CF_2Br_2 molecules. The absorption cross section for CF_2Br_2 is taken to be 6.4×10^{-19} $cm^2\,molecule^{-1}$.[18,23)] The CF_2Br absorption cross section value is taken to be 6.2×10^{-19} $cm^2\,molecule^{-1}$ as measured by GTL. Using the σ_1 and σ_2 values, the CF_2 yield coming from secondary photodissociation as a function of laser fluence has been calculated from 0.1 to 10 $J\,cm^{-2}$ and is shown in Fig. 3. This shows that up to about 0.5 $J\,cm^{-2}$ the CF_2 yield from secondary photodissociation is not significant. However, with increasing fluence the yield increases sharply and at about 5 $J\,cm^{-2}$ as much as 90% of the CF_2Br radicals will undergo secondary photodissociation to give CF_2. The

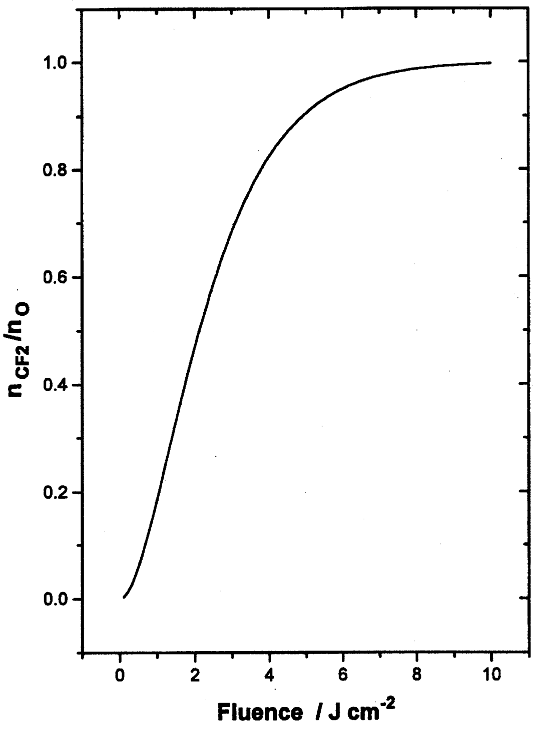

Fig. 3. CF_2 yield due to secondary photodissociation of CF_2Br as a function of laser fluence.

curve demonstrates that depending on the laser fluence the relative yield of CF_2 and CF_2Br will change. The figure also shows that in the fluence region of 0.5—3 J cm^{-2}, the CF_2 yield is almost linear. This is in accordance with the molecular beam results of KZBL, where they found nearly linear production of CF_2 radicals in the fluence range 0.08 to 2.5 J cm^{-2}. From this figure one can estimate the extent of secondary photodissociation in the experiments of KZBL. At a fluence of 2.5 J cm^{-2} used by them, about 60% of the CF_2Br radicals will undergo secondary photodissociation to give CF_2. The linear dependence of fluorescence intensity on laser fluence in the region of 0.12—1.2 J cm^{-2} as reported by Sam and Yardley[20] can also be explained from this figure. These results show that under low laser fluences (<0.5 J cm^{-2}) the main decay channel for transient CF_2Br is dimerization. However, with increasing laser fluence the secondary photodissociation of CF_2Br to give CF_2 starts competing with the recombination channel.

This kinetic scheme for our fluence conditions (0.25 J cm^{-2}) accounts for ca. 2% of the CF_2 generation due to secondary photodissociation of CF_2Br. In our experiments C_2F_4, 11% of the total CF_2Br_2 dissociated was detected among the final products. This will correspond to a maximum of 22% transient CF_2 yield, assuming all C_2F_4 comes from the dimerization of transient CF_2. If all the CF_2 were generated due to secondary photodissociation, it should have evolved very fast (on a picosecond time scale). To check for the relative contribution of CF_2 in the transient absorption spectrum, absorbance was measured at 249 nm. At 2 μs the total absorbance (at 249 nm) due to CF_2 and CF_2Br is about 8 times less than what will be expected on the basis of 22% CF_2 yield alone (using $\sigma(CF_2)=2.9\times10^{-17}$ cm^2 molecule^{-1} at 249 nm, Ref. 28). Considering all errors to their maximum extent in our experiments we can account for a maximum of 4% CF_2 with the observed absorbance at 2 μs. Further if we assume that 22% of the CF_2 is generated by unimolecular dissociation of CF_2Br before 2 μs, in that case the UV spectrum at 2 μs should have another peak with $\lambda_{max}\approx249$ nm, which was not observed. Spectra measured at longer delay times also showed no increase in the absorbance, thus showing that CF_2 is not produced even at longer time scales. This observation implies that unimolecular decay of CF_2Br to CF_2 does not occur to any significant extent. This is in agreement with the molecular beam results of Ref. 22 where spontaneous decay of CF_2Br was not observed to any significant extent. Thus, it follows that in our experiments CF_2 is not the source of the C_2F_4 that is observed as the final product. CF_2 produced as a result of secondary photodissociation can account for only 1% of the C_2F_4. It is possible that a reaction of the following type may be occurring in the system.

$$CF_2Br + CF_2Br \rightarrow C_2F_4Br_2^* \tag{8}$$

$$C_2F_4Br_2^* \rightarrow C_2F_4 + Br_2 \tag{9}$$

The activation energy for reaction 9 is not known. The enthalpy of reaction 9 is calculated to be about 161 kJ mol^{-1}.[30] The activation energy for elimination of Br_2 from 1,2-dibromopropane has been reported to be about 184 kJ mol^{-1} [31] and in this case also may not be very different. The average and the maximum internal energy of CF_2Br radicals produced as primary products have been shown to be 71 and 117 kJ mol^{-1} for Br($^2P_{1/2}$) as the co-product and 117—163 kJ mol^{-1} for Br($^2P_{3/2}$) as the co-product.[22] When two such radicals combine, the resultant $C_2F_4Br_2$ will have a minimum of 142—326 kJ mol^{-1} energy associated with it in addition to the enthalpy of reaction (Eq. 8). Most of these may be stabilized due to collisions and are observed as stable products. However, some of these energized $C_2F_4Br_2$ may undergo further reaction to give $C_2F_4+Br_2$.

2. Absorption Cross Section of CF_2Br. Using the absorbance value, dissociation yield per pulse, and the path length (as described in Ref. 25), we estimated the absorption cross section of CF_2Br at 260 nm to be $(1.05\pm0.2)\times10^{-18}$ cm^2 molecule^{-1}. From the relative absorbance values at 248 and 260 nm in this study, the $\sigma_{(CF_2Br)}$ value at 248 nm is calculated to be $(5.1\pm1)\times10^{-19}$ cm^2 molecule^{-1} after correction for the 2% CF_2 yield in both these values. This value is the weighted mean of cross sections averaged over the internal energy distribution at 2 μs. Our $\sigma_{(CF_2Br)}$ value at 248 nm is an order of magnitude lower than the value reported in Ref. 32 (4.4×10^{-18} cm^{-2} molecule^{-1}) obtained by measuring the laser-induced fluorescence intensity of CF as a function of laser fluence and fitting the results to a kinetic equation with two unknown parameters. Using the cross section value of Ref. 32, if we calculate the CF_2 yield as a function of laser fluence for the secondary photodissociation of CF_2Br, then for our fluence conditions the CF_2 yield comes out to be 6—7%. In such a case the transient spectrum would have shown another peak at 249 nm that was not observed experimentally. Apart from this, the value of 6% is 50% higher than what can be permitted even considering the maximum error in our absorbance measurements. Further, the CF_2 yield obtained using this value does not show linear behavior in the fluence range 0.08—2.5 J cm^{-2}, contrary to the observations of KZBL. However, the cross section value reported by GTL and by us explains both these observations. The value in case of Ref. 32 probably represents the absorption cross section of those CF_2Br radicals which give CF radicals and not the average cross section value.

3. Kinetics of CF_2Br Radicals. The growth of the absorption signal was found to be limited by the response time of the detection system. It has been suggested that 248 nm irradiation leads to direct photodissociation,[23] and hence the dissociation rates should be very fast in agreement with the experimental observation. The decay of the transient absorption signal has been used to find out the dimerization rate constant of the CF_2Br radical. A plot of $(\mathrm{absorbance})^{-1}$ vs. time (Fig. 4) is found to be linear, indicating that the decay kinetics is of second order. The kinetics is in agreement with the observed product $C_2F_4Br_2$ also. The slope of this plot gives $k/\sigma \cdot l$, where k is the second order rate constant, σ is the absorption cross section at the monitoring wavelength, and l is the path length. Fitting these values into the expression we get rate constant for CF_2Br dimerization to be $(3.0\pm0.6)\times10^{-12}$ $\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. The value is in agreement with that observed in Ref. 24.

Conclusion.

A transient absorption spectrum in the range of 200—320 nm with $\lambda_{\mathrm{max}}\approx260$ nm has been observed in the 248 nm photodissociation of CF_2Br_2. This has been assigned to the primary photodissociation product CF_2Br radical. The absorption cross sections of this radical at 260 and 248 nm have been determined to be $(1.05\pm0.2)\times10^{-18}$ and $(5.1\pm1)\times10^{-19}$ $\mathrm{cm^2\,molecule^{-1}}$, respectively. The rate constant for CF_2Br dimerization has been calculated to be $(3.0\pm0.6)\times10^{-12}$ $\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

The authors thank one of the referees for his valuable suggestion.

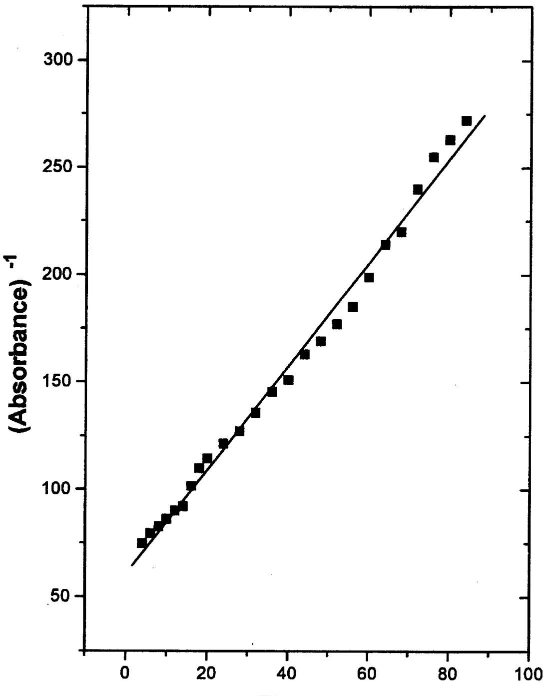

Fig. 4. Plot of $(\mathrm{Absorbance})^{-1}$ vs. Time for CF_2Br recombination.

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