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Photodissociation of trifluoroacetic acid at 193 nm: Mechanism for formation of OH radical and stable products

Sumana SenGupta*, Ankur Saha, Awadhesh Kumar*,[1], Prakash D. Naik[1]

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

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ABSTRACT

Trifluoroacetic acid (TFA) is released in the atmosphere through its use in the chemical industry and as degradation product of chlorofluorocarbon (CFC) alternatives like hydrofluorocarbons and hydrochlorofluorocarbons. In the present study, we have investigated the OH formation dynamics in the photodissociation of TFA at 193 nm by Laser Photolysis-Laser Induced Fluorescence (LP-LIF) method, as well as stable product formation by GC−MS and FTIR. It was found that, ~26% of the available energy is partitioned into the relative translation of the photoproducts *(f(T)* = 0.26*)*, which could be explained by presence of an exit barrier of ~13 kcal/mol in OH formation channel. This result is very similar to OH formation from acetic acid (AA) and difluoroacetic acid (DFA), indicating fluorination at the side chain of aliphatic carboxylic acids does not significantly change the mechanism of C−OH bond scission. Our experimental results tallied with the theoretical studies, which suggested that the major OH formation channel in acetic acid and fluoroacetic acid is direct dissociation from the optically excited S_1 state through an exit barrier, with some competition from the T_1 state. However, quantum yield of OH formation from TFA (0.4) was found to be much smaller than AA (0.8), which is probably caused by higher reaction barrier in T_1 state of TFA, compared to AA. CHF_3, C_2F_4, C_2F_6, CO_2, CO, CF_3CFO, CF_2O and hexafluoropropylene oxide (HFPO) were detected as the stable products of the photolysis of TFA. The theoretically optimized ground state dissociation channels showed significant difference between TFA and AA.

1. Introduction

Trifluoroacetic acid (TFA) is commonly used in the chemical industry as synthetic as well as analytical reagent [1,2]. It has also been identified as the end product of the atmospheric degradation of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and long chain poly fluorinated compounds (PFCs) which are used as CFC alternatives [3–5]. A very small contribution to the environmental TFA can also come from the biological or atmospheric oxidation of anesthetics like halothane and isoflurane [6,7]. To assess the environmental impact of TFA and other fluorinated carboxylic acids, their gas-phase dissociation has been extensively investigated [8–16]. The dissociation of TFA, by different methods like thermolysis [8–10], pyrolysis [11], IRMPD [12] and photodissociation [13,9–16] is already reported. It is also been established that, decarboxylation and dehydration are the major photodissociation channels at lower wavelengths (190–220 nm) [17,18] for acetic acid (AA), but not in case of difluoroacetic acid (DFA). Rather, γ-elimination of hydrogen fluoride was found to be the most important channel in thermal decomposition, IRMPD and UV laser photolysis of DFA [9,16]. But the dynamics for OH formation by photodissociation at 193–220 nm, is reported to be similar in case of carboxylic acids [17–20], and fluoroacetic acids [13–15,21]. For both fluorinated and non-fluorinated carboxylic acids, earlier, it was proposed that the initially populated S_1 state undergoes radiationless transition to a nearby triplet state, and the OH generation channel takes place from both the triplet and singlet states, the former being more dominant. Accordingly, in the previously reported comparison between the OH formation from photodissociation of TFA and AA at 193 nm, the results were discussed assuming that major channel operates predominantly from the T_1 state, with some contribution from the S_1 state [14]. However, in the more recent theoretical studies [17,22], it was found that in case of fluorinated carboxylic acids, OH formation from the S_1 state itself is one of the major channels.

Since the current theoretical studies predict the mechanism to be quite different, it is important to re-evaluate the dynamics of OH formation from TFA. In order to understand the actual nature of the

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* Corresponding authors.
E-mail addresses: sumansg@barc.gov.in (S. SenGupta), awadesh@barc.gov.in (A. Kumar).

[1] Also affiliated to Homi Bhabha National Institute, Anushaktinagar, 400 094, Mumbai, India.

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potential energy surface for dissociation, we have investigated the OH formation dynamics, as well as stable product formation in the photodissociation of TFA by 193 nm laser. To form a comprehensive idea about the dissociation mechanism, we have compared our results with the current theoretical studies in details. To determine the actual effect of fluorination on the photodissociation mechanism of carboxylic acids, the results were also extensively compared with that of AA and DFA. Theoretical calculations for dissociation from both the ground state and the excited states were discussed to support our experimental results.

2. Method and methodologies

2.1. Experimental

Trifluoroacetic acid (> 99.0% purity) was procured from Sigma Aldrich and used after repeated freeze-pump-thaw cycles. Its dissociation was studied using the Laser Photolysis–Laser Induced Fluorescence technique. The experimental set-up is same as that described in our previous article [23]. Briefly, the photolysis was effected by an excimer laser (Lambda Physik, Model Compex-102, Fluorine version), and the product OH was probed by a Quantel dye laser, with frequency doubling and the mixing module (TDL 90), pumped by a Quantel seeded Nd:YAG laser (model YG 980 E-20). The reaction chamber was made of glass with crossed arms at right angles, provided for the entrance of the pump and the probe laser beams, which intersect at the center of the reaction chamber. The detection system was attached to the bottom window, to capture a view of the intersection volume of the photolysis and the probe lasers. This system consisted of a lens (focal length 50 mm, diameter 38 mm) to collect the fluorescence, a photomultiplier tube (Hamamatsu, model R 928P) to detect it, and a band pass filter (λ_{centre} = 310 nm, FWHM = 10 nm, $\%T_{310nm}$ = 10%) placed between them to cut off the scattering from the photolysis laser light. The fluorescence signal was gate integrated by a boxcar (SRS 20), averaged over 30 laser shots, and fed into an interface (SRS 245), for A/D conversion. The dye laser output was scanned by a PC via an RS232 interface, and the same was used to collect the data through a GPIB interface, using a control and data acquisition program. LIF intensities were normalized with respect to both the pump and the probe laser energies, using suitable photodiodes, to correct for the laser intensity fluctuations.

The vapour of the compound (at a pressure of ~10 mTorr) was flowed through the reaction chamber at a flow velocity of approximately 10 cm/s, and was photolysed by ArF laser at 193 nm. The OH fragment was probed state selectively by exciting the $A^2\Sigma \longleftarrow X^2\Pi$ (0,0) transition of OH (306–309 nm), and monitoring the subsequent $A \rightarrow X$ fluorescence. Both the laser beams were unfocussed and attenuated, to prevent any saturation effect or multiphoton event. LIF signal was found to be linearly proportional to the laser powers. The linearity of the LIF signal also ruled out any interference from TFA dimer, which, anyway is unlikely to form under such low pressure and high flow velocity.

Absorption cross section of TFA was measured by filling a known pressure of the sample into a 50 cm long cylindrical absorption cell, fitted with MgF_2 windows at both ends, and placing it in the excimer laser beam. TFA is known to form dimer at room temperature, hence, pressure was kept very low (between 2–5 torr) to minimize dimer formation. Sample pressure in the cell was measured with a capacitance manometer. A beam splitter was placed in front of the cell for dividing the original laser beam into two parts, one for passing through the sample and the other as a reference. Two photodiodes were used for measuring the intensities of the sample beam, after exit from the sample cell and the reference beam. By measuring ratio of the intensities of the two beams, fraction of the intensity absorbed by the sample was determined. This fraction was plotted against the number of molecules in the cell in a semilog plot. Within the experimental range of pressures, the relation was found to be linear, thus overruling any significant contribution of dimers. Using Lambert-Beer's law, absorption cross section of TFA molecule at 193 nm was calculated. This value was used for determination of the quantum yield of the OH formation channel from TFA on excitation at 193 nm.

A stainless steel cell, with crossed arms at right angles to each other, and fitted with suitable windows, for allowing UV and IR light, was used for both Gas Chromatography–Mass Spectrometry (GC—MS), infrared fluorescence (IRF) and FTIR studies. The cell was filled with TFA (around 1 Torr) and photolysed by about 1000 pulses of 193 nm laser with the average pulse energy of about 4–5 mJ, and the IRF was collected and measured at discrete wavelengths, using appropriate band pass filters. The emission was detected at right angle geometry by a liquid N_2 cooled InSb detector (IS-2.00 Graseby), equipped with a matched pre-amplifier. The output signal was fed to a Lecroy (9350 A) digital oscilloscope, for digitization, averaging and background subtraction. The same irradiated sample was used for recording the FTIR absorption spectrum by a Bruker IFS 66v/S FTIR instrument, and the stable products were analyzed qualitatively by separating with Q-plot column, employing GC—MS (Chemito GC 8610).

2.2. Theoretical calculations

To understand the complete implications of the experimental results, theoretical calculations were done using Gaussian 03 suite of programmes [24]. To compare the dissociation energy of C—OH bond from the for AA, DFA and TFA, the ground state structure of these three molecules and the products C—OH bond breaking were optimized at MP2/6-311++G** level. The energies of the optimised structures were also calculated at the same level and the C—OH bond dissociation energy ($D_0 = h\nu - E_{avl}$) were determined.

To gain complete information about the overall dissociation process of TFA, we evaluated its ground state dissociation channels theoretically at MP2/6-311++G** level of theory. All the relevant stationary structures and transition states were geometry optimized and their energies were calculated at the same level.

The equilibrium geometry of the lower excited electronic states (S_1 and T_1) was optimised at the CIS/aug-cc-pvdz level and these geometries as well as energies were used for obtaining the vertical excitation energies for various transitions. The nature of the orbitals involved in the transition effected by absorption at 193 nm was obtained at this level. To find the nature of the lower energy excited states, potential energy curves for the ground state (S_0) and the first singlet and triplet (S_1 and T_1) of TFA was mapped at the time-dependent B3LYP/6-311++G** level as a function of the C—OH bond length. The geometry was frozen to the equilibrium position of the respective states except for variation in the C—OH bond length.

Results of these theoretical calculations are discussed in the relevant sections.

3. Results

3.1. Detection of OH on excitation of TFA at 193 nm

The UV photolysis of TFA at 193 nm leads to formation of OH radical as a transient radical product which was detected by its LIF signal. The state selective distribution of the nascent OH radicals was probed by measuring fluorescence of the A-X(0,0) system, after exciting the same system with frequency doubled tunable dye laser. Similarly, an attempt was made to measure the product OH ($v'' = 1, J''$) by exciting the A-X(1,1) transition, but no detectable signal was observed. Thus, OH formed in higher vibrational levels ($v'' > 0$) is negligible, i.e., the OH generated was found to be vibrationally cold. Several rotational lines were measured (shown in Fig. 1), to obtain information about the OH formation dynamics.