

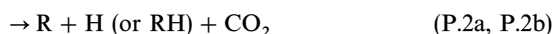
Products of the ultraviolet photodissociation of trifluoroacetic acid and acrylic acid

Michael C. Osborne, Qiang Li and Ian W. M. Smith*

School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

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The photodissociation of trifluoroacetic and acrylic acids by the ultraviolet light from a flashlamp has been investigated by measuring the relative yields of some of the major products by time-resolved infrared absorption using tunable, narrow band diode lasers. Yields of CO₂ were measured both in the absence and presence of added O₂. The former experiments measure the CO₂ produced directly by decarboxylation of the acid, channel (2) below, the latter the sum of the yields from channels (1) and (2) since HOCO is rapidly converted to CO₂. The yields of CO from the decarbonylation channel (3) have also been measured.

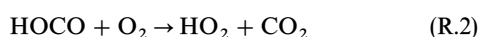


For trifluoroacetic acid, the relative yields are found to be [HOCO] : [CO₂] : [CO] = (0.28 ± 0.07) : (0.61 ± 0.09) : (0.11 ± 0.06) and, for acrylic acid, [HOCO] : [CO₂] : [CO] = (0.32 ± 0.08) : (0.37 ± 0.08) : (0.31 ± 0.09). The results are discussed in relation to the other, limited, measurements on the photodissociation of these acids and whether these three processes are likely to occur independently of one another.

In recent years there have been a number of spectroscopic^{1,2} and kinetic^{3,4} studies of HOCO radicals in which they were generated by photodissociation of a carboxylic acid, usually acrylic acid (CH₂=CHCOOH). The HOCO radical is a transient intermediate in the important reaction between OH radicals and CO,⁵⁻⁸ and in the reverse reaction,



and can indeed be stabilised in the case of the forward reaction, if the total pressure in the system is sufficiently high.^{9,10} Amongst other results, measurements on the reactions of HOCO have shown it to react rapidly with O₂.^{3,4,11}



Determinations of the rate constant for this reaction yield values of *k*₂ varying from 1.45–1.9 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ at 298 K.^{3,4,11} One conclusion of these measurements is that the nett result of reaction between OH and CO in the atmosphere is to yield HO₂ + CO₂, either *via* reaction (R.1) plus the combination of the H atom product with O₂ or *via* the stabilisation of the HOCO formed from OH + CO followed by reaction (R.2).

In contrast to this rather well-understood situation, many of the important details of the ultraviolet photodissociation of the carboxylic acids are not well-known and there have been relatively few experimental studies of these processes using modern techniques. Among the photodissociation channels that have been postulated are



The thermodynamics of these and other photodissociation channels in trifluoroacetic and acrylic acids are given in Table 1.

The first study of the photolysis of trifluoroacetic was carried out by Mearns and Back in 1963.¹² They used a continuous medium pressure mercury arc to photolyse the acid between 200 and 220 nm. The acid vapour pressure was varied between 10 and 100 Torr and the temperature between 90 and 190 °C. The major products were CO₂ and C₂F₆ with smaller yields of CO, H₂ and CF₃H. To examine the mechanism further, Mearns and Back analysed the products of the photoinitiated reaction in the presence of isobutane, C₄F₁₀ and but-1-ene. C₄F₁₀ had only a minor effect on the product yields, suggesting that the relaxation of vibrationally excited species was not the cause of the marked changes which occurred when isobutane or but-1-ene was added. The presence of C₂F₆ and its replacement by CF₃H in the presence of isobutane appeared to establish the production of CF₃ radicals in the primary photochemical process beyond doubt, although all three processes (P.1), (P.2a) and (P.3a), with R = CF₃, yield CF₃.

Largely on the basis of the effects of added isobutane and but-1-ene on the yields of CO₂ and CO, Mearns and Back postulated that the C—C bond fission represented by eqn. (P.1) was the principal primary photochemical process. Of course, the evidence for the production of HOCO radicals was only indirect and the characterisation of (P.1) as the major photodissociation channel for trifluoroacetic acid on the basis of these experiments is open to some doubt. However, before the present investigation, there had been no direct study of the photodissociation of trifluoroacetic acid reported in the literature.

As mentioned earlier, the photodissociation of acrylic acid has been the usual source for spectroscopic and kinetic studies of the HOCO radical. In addition, there have been a few recent studies of the photodissociation itself, though none has

Table 1 Thermodynamics of different channels in the photodissociation of trifluoroacetic and acrylic acids

Products	R = CF ₃		R = CH ₂ =CH	
	$\Delta_r H/\text{kJ mol}^{-1}$	$\{\Delta_r H - (N_A hv)\}/\text{kJ mol}^{-1}$	$\Delta_r H/\text{kJ mol}^{-1}$	$\{\Delta_r H - (N_A hv)\}/\text{kJ mol}^{-1}$
R + HOCO	+339	-231	+414	-156
R + H + CO ₂	+385	-185	+461	-109
RH + CO ₂	-60	-630	-4	-574
R + OH + CO	+489	-81	+565	-5
ROH + CO			+89	-481
RCO + OH			+435	-134
RCHO + O			+496	-73

For each acid, the first column shows the standard enthalpy change for transformation of RCOOH to the stated products at 298 K. The second column shows the enthalpy change associated with photodissociation by photons of wavelength of 210 nm ($N_A hv = 596.6 \text{ kJ mol}^{-1}$).

had the determination of the branching ratios into different product channels as their primary aim.

Rosenfeld and Weiner¹³ looked for infrared fluorescence following the pulsed excimer laser irradiation of acrylic acid at 193, 248 and 308 nm. No emission was detected at the longest wavelength. At the two shorter wavelengths, emission at 4.3 μm , corresponding to the ν_3 band region of CO₂, was observed and experiments with cold gas filters showed that a substantial fraction of the emission came from levels with $\nu_3 > 1$. Rosenfeld and Weiner could detect no emission in the C—H stretching region (*ca.* 3.3 μm) or from CO at 4.8 μm . However, in assessing these results, it is necessary to remember that the Einstein coefficients for these different systems differ appreciably, with that for the (00⁰1–00⁰0) band of CO₂ *ca.* 14 times that for the (1, 0) band of CO. Rosenfeld and Weiner concluded that decarboxylation, *i.e.* channel (P.2), is a major process and forms CO₂ excited in the ν_3 vibration.

Lessard¹⁴ followed up the work of Rosenfeld and Weiner using time-resolved infrared absorption in a manner similar to that reported in the present paper. Searches were made for both CO and CO₂ following laser photolysis of CH₂=CHCOOH at 193 and 248 nm. CO was only observed using the shorter wavelength, though in assessing this result and those of Rosenfeld and Weiner, one should note that acrylic acid has only a very small absorption cross-section at the longer wavelength¹⁵ and therefore any concentration of vibrationally excited CO might have been below their detection limit. Prompt formation of CO₂ was observed at both wavelengths, suggesting its production in a primary process.

The most dynamical study to date of the photodissociation of acrylic acid is that performed by Kitchen *et al.*¹⁶ in a crossed laser-molecular beam apparatus. Products were detected by mass spectrometry using 200 eV electron impact ionisation. The measured mass peak at $m/e = 44$ was attributed entirely to the CO₂⁺ daughter ion of HOCO. Kitchen *et al.* concluded that, at 193 nm, neither decarboxylation, channel (P.2), nor decarbonylation, channel (P.3), is important and that only C—C bond scission, channel (P.1), and C—O bond fission leading to CH₂=CHCO + OH are significant photodissociation channels.

Finally, in this survey of previous work, we mention the work of Miyoshi *et al.*⁴ Although their primary aim was to make kinetic measurements on reactions of HOCO using a time-resolved mass spectrometric technique, they used photodissociation of acrylic acid to generate HOCO and they observed how the concentration of HOCO changed with time both in the presence and absence of added co-reagent. Because they used photoionisation with $h\nu \equiv 10.03 \text{ eV}$, they could observe only a limited range of species, and peaks at $m/e = 44$ and $m/e = 55$ were assigned to C₂H₃OH and C₂H₃CO, respectively. It was further suggested that the decay of HOCO in the absence of any added reagent at a rate which was both non-exponential and dependent on total pressure represented competition between unimolecular dissociation

and relaxation of vibrationally excited HOCO radicals. The rates involved mean that the dissociation would have to be due to tunnelling through the barrier leading to H + CO₂. This suggestion is further discussed later in this paper.

In the experiments described in the present paper, we have used a time-resolved infrared absorption technique to determine the branching ratios into channels (P.1), (P.2), and (P.3) when trifluoroacetic acid (R = CF₃) and acrylic acid (R = CH₂=CH) are photolysed by the output from a conventional flashlamp. To measure the relative yields of HOCO and CO₂, absorbances on lines in the (00⁰1,00⁰0) band of CO₂ were measured in the presence and absence of O₂, HOCO being converted rapidly to CO₂ by reaction (R.2) when O₂ was added. The background source for these measurements was a diode laser tuned to the centre of an appropriate line in the ν_3 fundamental band of CO₂. Separate measurements, using a second diode, were carried out on the CO produced in channel (P.3). In all cases, the absorbances were measured at delays sufficient to ensure that both reaction (R.2) and the relaxation of any vibrationally excited CO₂ and CO were complete.

Experimental method

Fig. 1 provides a schematic of the apparatus used in the present experiments. Weak mixtures of the carboxylic acid in helium or argon were passed through a tubular reactor of 18 mm internal diameter. The central portion of this tube is made of Spectrosil quartz and a length of *ca.* 80 cm is surrounded by an annular flash lamp. The tube is fitted at both ends with CaF₂ windows which are set at 35° to minimise any effects due to back reflection of the radiation from the diode laser.

The annular space between the outer surface of the Spectrosil reactor and the outer quartz sleeve of the flashlamp is *ca.* 8 mm thick and is filled with *ca.* 10 Torr of xenon. Using 'O'-rings, this volume is sealed by brass end-pieces which also serve as the electrodes for the flashlamp. The flashlamp forms part of a custom-built charging circuit which includes two 0.5 μF , 20 kV capacitors and a power supply capable of charging at a rate of 1 kJ s⁻¹. The capacitor is generally charged to between 13 and 17 kV yielding a dissipated energy of between 85 and 145 J when the lamp is fired. The lamp was fired at rates between 0.6 and 1.0 Hz. To ensure that there was no build up of products, the gas flow was adjusted so that the reaction cell was re-filled twice during the period between flashes.

In the present experiments, the main disadvantage of using a flashlamp rather than a pulsed laser to effect photodissociation was the lack of definition of the energy of the photons absorbed by the molecules of carboxylic acid. Thus, photolysis occurs over a range of wavelengths with a distribution of input energies which is the result of the overlap of lamp output, limited at short wavelengths (*ca.* 165 nm) by the transmission of Spectrosil quartz, with the absorption spec-

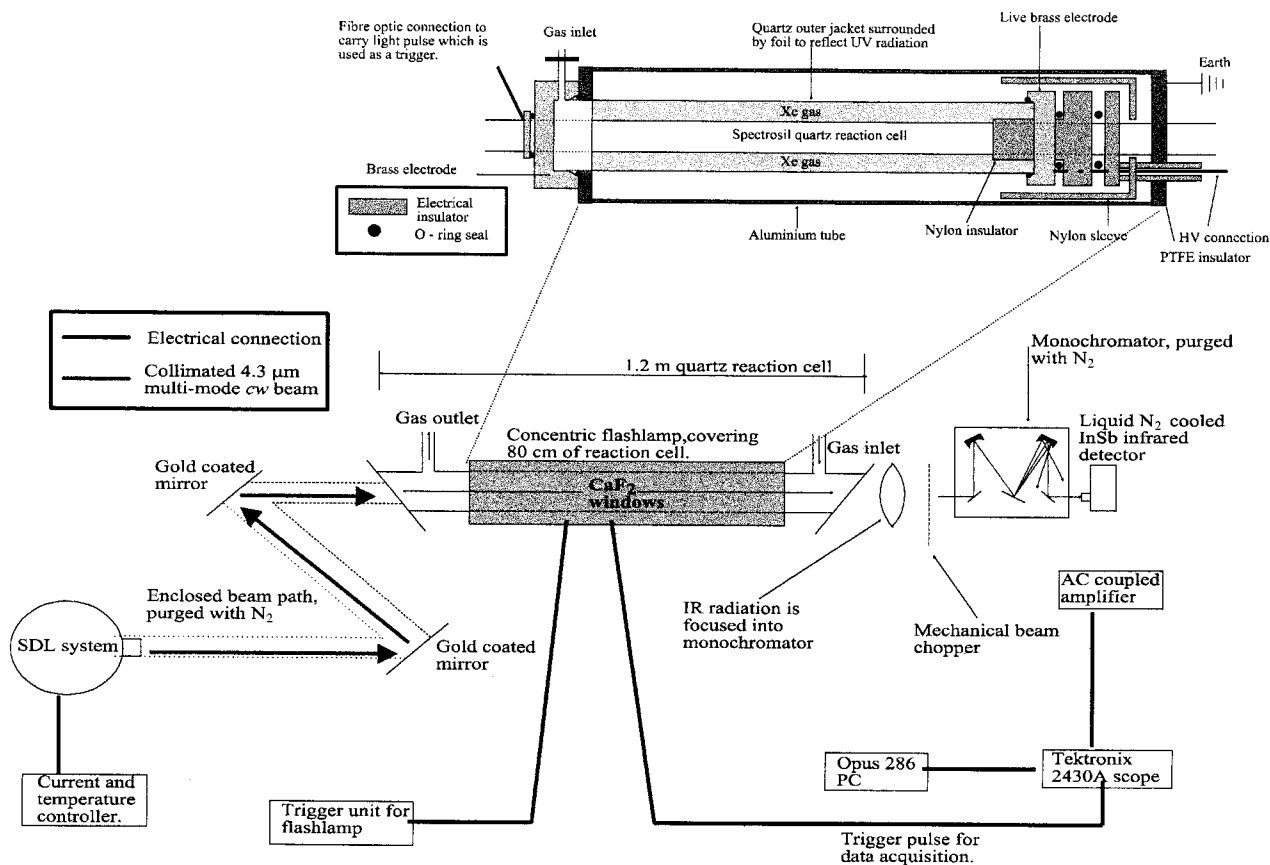


Fig. 1 Apparatus used to study the products of the ultraviolet photodissociation of trifluoroacetic and acrylic acids using time-resolved infrared absorption spectroscopy.

trum of the acid. We shall return to this point in the Discussion section of the paper. As, in the present work, the aim was to compare the yields of final products, the timescale of the measurements was quite long (see below) and consequently the longer duration of the light output from the lamp (measured as about 10 μ s) compared with a laser was unimportant. One advantage of a flashlamp is that it provides rather uniform illumination of the reaction volume, thereby minimising effects resulting from diffusion of the species being observed.

The tunable, infrared 'probe' radiation is provided by a liquid N₂ cooled diode laser system (Mutek GmbH, MDS 1150). Two different diodes (one for measurements on CO₂, one for measurements on CO) were employed in the experiments that are reported here. Because of the divergence of the radiation from a diode laser, collimating optics must be employed to generate a suitable probe beam. The collimating optics that were used originally (Mutek GmbH, MDS 1125) consisted of a total of five gold-coated mirrors, 3 planar, 1 ellipsoidal and 1 toroidal, mounted on a moveable stage. This arrangement produced a collimated beam of *ca.* 14 mm diameter and a divergence of about 1.5 mrad. It was later replaced by a single 90° off-axis parabolic mirror which gave a beam of similar diameter and divergence but much improved intensity, leading to better signal-to-noise. After the probe beam emerges from the reaction vessel, it is focused onto the entrance slit of a monochromator (Hilger-Watts, D330) which is fitted with a diffraction grating blazed at 6 μ m. This monochromator is able to select a single mode from the diode laser which is directed onto a liquid N₂ cooled InSb photovoltaic detector (Infrared Associates) placed at the exit slit of the monochromator. Because of the presence of CO₂ in the atmosphere it is essential to enclose and purge the complete path of the probe laser. This is done using N₂ from a cylinder. An AC coupled amplifier was used in conjunction with a cooled InSb

detector and the output from the amplifier was passed to a digital storage oscilloscope. Generally *ca.* 20 traces were averaged before subsequent processing. The time response of the detector-amplifier combination was about 10 μ s in the experiments that are reported in the present paper.

The output frequency of the diode laser could be estimated within a few wavenumbers using the monochromator. However, to find the frequency to the accuracy required it was necessary to use low pressures of one or more calibration gases, either in the reaction vessel or in a separate cell, together with a high finesse germanium transmission etalon (Mutek GmbH, MDS 1920). The calibrant gases used were CO₂, CO, OCS and N₂O (including their isotopomers). The infrared absorption frequencies of these gases have all been assigned, tabulated and provided in diagrammatic form.^{17,18} Of course, in the present work, tuning of the diode lasers for time-resolved absorption measurements was made easier by the fact that we were observing stable species (CO₂ and CO) in levels with high thermal populations.

The reaction cell and flashlamp are attached to a standard gas handling line constructed from Pyrex and fitted with greaseless stopcocks. All flows of gases were set using mass flow controllers (MKS and Bronkurst Hi-Tec). The helium or argon carrier gas was taken directly from a cylinder, He (Air Products, GC grade) and Ar (Air Products, Resolution grade), and was used without further purification. Oxygen was also delivered directly from a cylinder (BOC, 99.6%).

Different methods of delivery had to be used for the two carboxylic acids. The vapour pressure of trifluoroacetic acid is sufficiently high that dilute mixtures could be prepared with the carrier gas in a 20 l bulb and a controlled flow could be delivered using an appropriate mass flow controller. In contrast, because of its low vapour pressure at room temperature (only 3.5 Torr), acrylic acid was delivered using a bubbler followed by a cold trap. By controlling the temperature of the

cold trap, and hence the partial pressure of the acid at this point, and the flow of carrier gas through this line, it was possible to control the partial pressure of the acrylic acid in the reaction cell. Each new sample of acid was degassed by bubbling helium through it.

In calculating the amount of carboxylic acid in the reaction cell and the fraction of the acid present as monomer, it was necessary to allow for dimerisation. For trifluoroacetic acid, the equilibrium constant for $\text{dimer} \rightleftharpoons 2 \text{ monomer}$ is known to be $K_p = 4.14 \text{ Torr}$.¹⁹ Thus at 300 mTorr, the highest pressure used in the present experiments, 6.3% of the species are dimers. Allowance also had to be made for the higher fraction of dimers present in the trifluoroacetic acid originally measured into the storage bulb from which acid was delivered.

The corresponding equilibrium constant for acrylic acid is not known. We estimate a value of $K_p = 2.6 \text{ Torr}$ based on a comparison of K_p with $\text{p}K_a$ values for a sequence of carboxylic acids. Here, experiments are reported for pressures of acrylic acid up to 95 mTorr where 3.5% of the molecules are dimers. Again allowance was made for the higher fraction of dimers present in the flow line through which acrylic acid was admitted.

Further details of the equipment and methods used in the present experiments are available elsewhere.²⁰

Results

Traces of transmitted intensity *vs.* time were recorded following the photolysis of trifluoroacetic acid and acrylic acid with the diode laser tuned to the central frequency of the P(2), 2347.576 cm^{-1} , and P(4), 2345.985 cm^{-1} , lines in the (00⁰1, 00⁰0) band of CO_2 . These signals were converted to absorbances and a few examples of the many traces that have been recorded are displayed in Fig. 2. In each of these diagrams, traces are compared for experiments in the absence of O_2 and in the presence of 0.5 Torr of O_2 .

The general form of all the traces that have been recorded is similar. Following a prompt rise, which on close examination seems of larger amplitude in trifluoroacetic acid than in acrylic acid, there is a more gradual rise to an eventual steady state value which we take to be a measure of the total yield of CO_2 under the conditions of the experiment. The slow rise from the prompt signal to the absorbance at long time is taken to reflect the finite time for relaxation of CO_2 molecules formed in vibrationally excited states. In addition, in the presence of O_2 , there is a delay in the conversion of HOCO formed in process (P.1) to CO_2 *via* reaction (R.2). However, in the presence of 0.5 Torr of O_2 , the first-order rate constant $k_{R.2} [\text{O}_2]$ is equal to *ca.* $3 \times 10^4 \text{ s}^{-1}$ indicating rapid reaction compared with the time taken for the absorbance to reach its long time value. The period of several milliseconds over which the absorbances remain constant at long delay times confirms that the stable product, CO_2 , is formed rather uniformly through the reaction cell, and that no CO_2 is formed by unaccounted for secondary chemistry.

Confirmation that vibrational relaxation is responsible for the delay in the measured absorbances reaching their final values is obtained if one considers the experimental conditions and the rate constants for relaxation by the various species present in the experimental mixtures. In most of the present experiments, helium was present to bring the total pressure to 10 Torr. (For reasons explained later, some measurements were carried out on mixtures diluted to 50 Torr in He.) Helium efficiently relaxes the ν_1/ν_2 vibrational manifold of CO_2 . Thus, for $\text{CO}_2(01^10)$, the rate constant for relaxation is equal to $1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,²¹ corresponding to a first-order rate constant of $3.7 \times 10^4 \text{ s}^{-1}$ at 10 Torr of He. This suggests that the gradual increase in absorbance is only due to CO_2 molecules excited in the ν_3 manifold which is not strongly coupled to the ν_1/ν_2 levels.

Both spontaneous emission and collisions with helium can make a significant contribution to the ν_3 relaxation. The Ein-

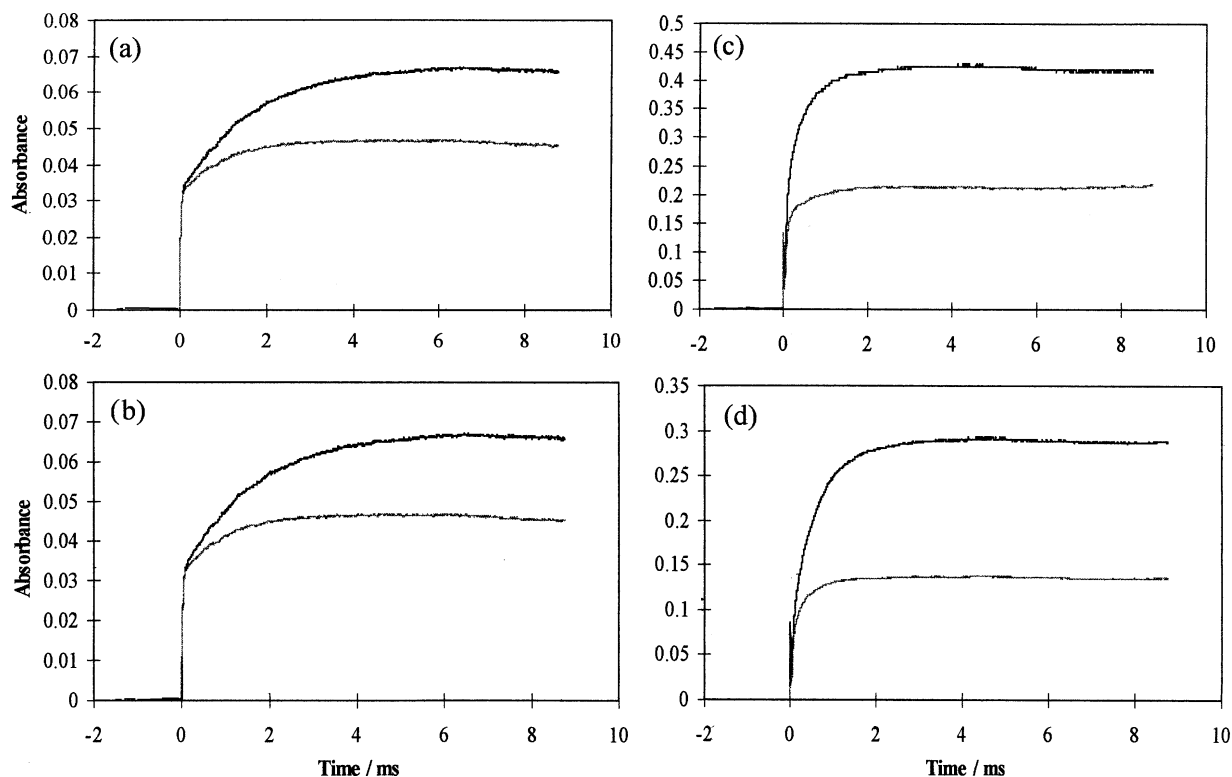


Fig. 2 Typical traces of absorbance *vs.* time for CO_2 formed in the presence (upper trace) and absence (lower trace) of 0.5 Torr of O_2 . All four measurements were made on the P(2) line of the (00⁰1,00⁰0) band of CO_2 , (a) 310 mTorr of trifluoroacetic acid; (b) 136 mTorr of trifluoroacetic acid; (c) 53 mTorr of acrylic acid; and (d) 25 mTorr of acrylic acid. All these experiments were carried out at a total pressure of 10 Torr in helium diluent. An absorbance of 0.1 on the P(2) line of the (00⁰1,00⁰0) band of CO_2 corresponds to a total CO_2 concentration of $9.3 \times 10^{12} \text{ molecule cm}^{-3}$.

stein coefficient for the former process is 420 s^{-1} .²² The second-order rate constant of relaxation by He is $2.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ yielding a pseudo-first-order rate coefficient of 770 s^{-1} at a helium pressure of 10 Torr. In the absence of any other relaxation channels, $\text{CO}_2(00^01)$ would have a relaxation time of *ca.* 0.84 ms. Measurements which will be described in a future publication^{20,24} yield rate constants for relaxation of $\text{CO}_2(00^01)$ by trifluoroacetic acid and acrylic acid of $(5.6 \pm 1.9) \times 10^{-12}$ and $(6.9 \pm 2.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The absolute value of these rate constants, and their similarity, suggest that relaxation may occur by vibration-to-vibration (V-V) transfer to the CO vibration in the acid.

The relative importance of the channels (P.1) and (P.2) yielding HOCO and CO_2 can be determined by comparing absorbances on a given $\text{CO}_2(00^01,00^00)$ absorption line at long delay times. Inspection of the traces in Fig. 2 shows: (a) that photolysis of acrylic acid gives higher absolute yields than that of trifluoroacetic acid (note the higher absorbances from smaller acid concentrations in the former case), and (b) that, in the presence of O_2 , a higher proportion of CO_2 comes directly from photolysis in the case of trifluoroacetic acid. The higher absolute yields from acrylic acid are consistent with its stronger absorption at the ultraviolet wavelengths above *ca.* 165 nm ²⁵ which are produced by the flashlamp and transmitted by the Spectrosil reaction vessel.

We have examined the yields of CO_2 as a function of both the partial pressure of acid and the pressure of added helium. The results are shown in Fig. 3. From these data, we calculate that, in the presence of O_2 , $(70 \pm 5)\%$ of the CO_2 from trifluoroacetic acid comes directly from photolysis, whereas this

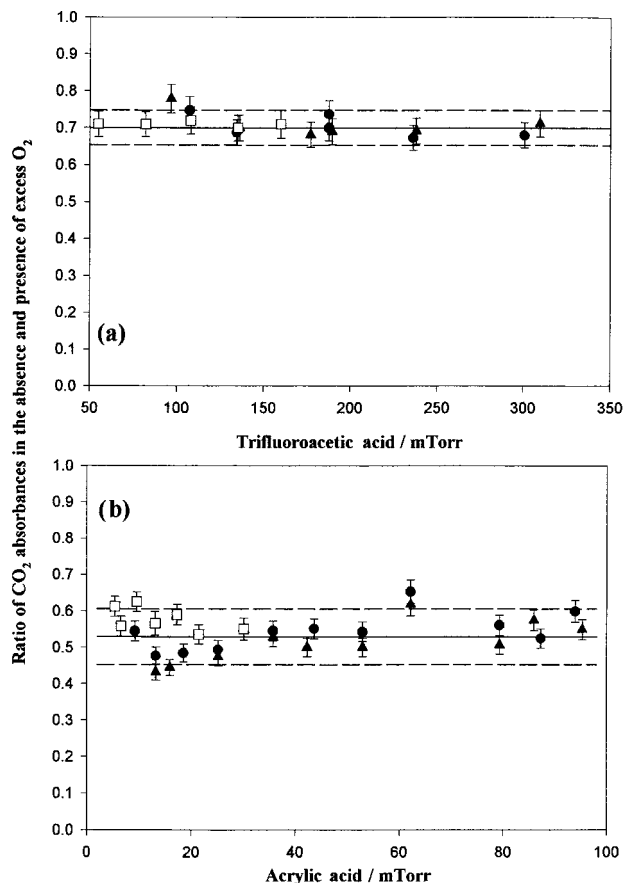


Fig. 3 Proportion of the CO_2 produced in the presence of added O_2 which can be attributed to direct formation in channel (P.2): (a) from trifluoroacetic acid, and (b) from acrylic acid. The closed symbols represent measurements made in 10 Torr of helium, the open symbols in 50 Torr of helium. The triangles are data derived from measurements on the $(00^01,00^00)$ P(2) line, the squares and circles from the $(00^01,00^00)$ P(4) line.

figure is $(53 \pm 8)\%$ in the case of acrylic acid. In both cases, the branching ratio was independent of the acid concentration and the total pressure over the ranges studied.

In order to examine the branching ratio into process (P.3), similar experiments to those just described for CO_2 were carried out on lines in the (1, 0) band, mainly on the R(8) line at 2176.284 cm^{-1} . Examples of the variation of absorbance with time following the photodissociation of trifluoroacetic acid and of acrylic acid are shown in Fig. 4. They show a similar form to the CO_2 traces: a prompt signal, followed by a slow rise to a final steady value. The poorer signal-to-noise, especially in the case of the trace from trifluoroacetic acid, is the result of three factors: the small yield of CO, the small absorption strength relative to CO_2 , and the noise from the firing of the flashlamp affecting the performance of the diode.

Again, the slow rise is attributed to the relaxation of CO from vibrational states above $v=0$. Comparison of the absorbance at long time with that measured promptly suggests that when trifluoroacetic acid is photolysed *ca.* 40% of the CO is produced in $v=0$, the remainder in levels with $v>0$. In the case of acrylic acid, these figures are approximately reversed with *ca.* 60% in $v=0$, 40% in $v>0$.

Vibrationally excited CO is notoriously impervious to collisional relaxation, at least by atomic collision partners. The first-order rate constants obtained by adding the Einstein

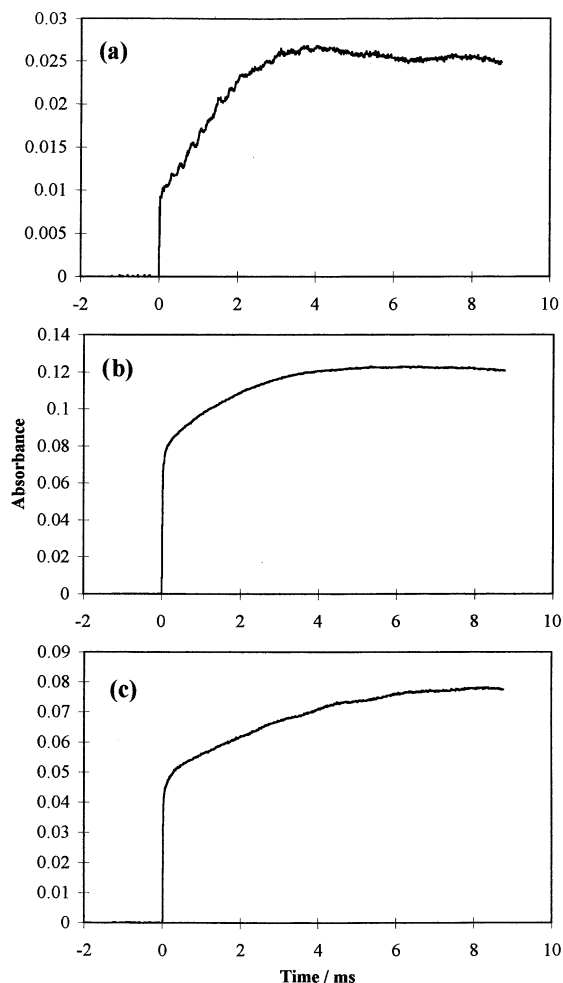


Fig. 4 Typical traces of absorbance *vs.* time for CO: (a) from 180 mTorr of trifluoroacetic acid measured on the (1, 0) P(5) line; (b) from 53 mTorr of acrylic acid measured on the (1, 0) R(8) line, and (c) from 25 mTorr of acrylic acid measured on the (1, 0) R(8) line. All these experiments were carried out at a total pressure of 10 Torr in helium diluent. An absorbance of 0.1 on the P(5) line of the (1, 0) band of CO corresponds to a total CO concentration of $1.4 \times 10^{13} \text{ molecule cm}^{-3}$; and absorbance of 0.1 on the R(8) line to a total CO concentration of $1.6 \times 10^{13} \text{ molecule cm}^{-3}$.

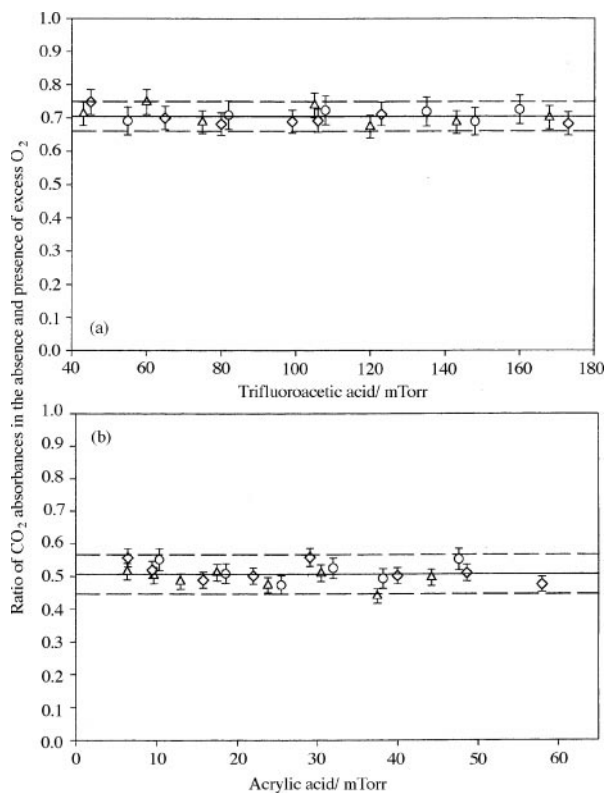


Fig. 5 Proportion of the CO₂ produced in the presence of added O₂ which can be attributed to direct formation in channel (P.2) in experiments performed with different energies dissipated through the flashlamp: (a) from trifluoroacetic acid, and (b) from acrylic acid. All measurements were made on the (00⁰1,00⁰) P(4) line. The flash energies were (Δ) 115 J, (◇) 33 J and (○) 21 J. In all cases the total pressure was 10 Torr.

coefficient for spontaneous emission²⁶ to the pseudo-first-order rate constant for relaxation by He²⁷ is only 34 s⁻¹. There seems little doubt that, in our experiments, relaxation of CO ($v > 0$) is dominated by collisions with the acid. This is consistent with the more rapid rise of absorbance with time evident in Fig. 4(b), 53 mTorr of acrylic acid, compared with 4(c), where the acrylic acid pressure is 25 mTorr. The form of the traces in Fig. 4 suggests that the rate constants for relaxation of CO ($v > 0$) by the two acids lie in the range 10⁻¹² to 10⁻¹³ cm³ molecule⁻¹ s⁻¹. Relaxation is again likely to occur by V-V transfer to the CO stretching mode in the acid.

Assuming the absorption lines to have a Doppler profile, the measured absorbances can be converted to concentrations of CO₂ and CO, using the well-established integrated intensities for the (00⁰1,00⁰) and (1, 0) bands in these molecules.²⁸ The resultant factors, which have been used to convert absorbances to concentrations, are given in the captions to Figs. 2 and 4. We found that absolute yields of CO₂ and CO do not scale linearly with the acid concentration in the case of either acid, which we attribute to the fact that absorption occurs over a range of ultraviolet wavelengths with different absorption cross-sections. The total observed product concentration, *i.e.* [HOCO] + [CO₂] + [CO], expressed as a fraction of the initial concentration of the acid is found from the measured yields of these products to be <5% in all cases and much less in most experiments. This figure can then be used to estimate the amount of energy released in the photochemical processes (P.1), (P.2) and (P.3), and in the HOCO + O₂ reaction when O₂ is present, and hence the consequent temperature rise. Assuming that photodissociation occurs only *via* channels (P.1), (P.2b) and (P.3b), based on the exothermicities given in the last column of Table 1, we estimate that any temperature increase is always less than 5 K. The assumption that channels (P.2) and (P.3) proceed to the molecular products,

rather than to the less exothermic radical products, means that our estimate of the temperature rise is an upper limit and confirms that thermal effects can be ignored in analysing our experiments.

Finally, we considered the possibility that all or some fraction of the observed CO₂ and CO products was formed by photodissociation of HOCO radicals created in the primary photolysis of the carboxylic acid. Unfortunately, there is no published ultraviolet spectrum of HOCO to aid in the assessment of this possibility. To test it experimentally, yields of CO₂ were measured in the presence and absence of added O₂ with different energies dissipated through the flashlamp. If photolysis of HOCO was producing significant concentrations of CO₂, this effect would be greatest at the largest flashlamp energies and the measured branching ratios would change as the flashlamp energy was varied. Fig. 5 shows results of these experiments on both trifluoroacetic and acrylic acid. In both cases, the branching ratio is invariant with the flashlamp energy and we conclude that photolysis of HOCO is not a significant source of CO₂ (and, by implication, of CO) under the conditions of our experiments.

Discussion

The present work seems to establish unequivocally that, for the photolysis wavelengths used in our experiments, photodissociation of trifluoroacetic acid and acrylic acid both proceed by at least three competing channels: (P.1) cleavage of the C-C bond to yield R + HOCO; (P.2) decarboxylation, *i.e.* loss of CO₂ with RH or R + H as co-products; and (P.3) decarbonylation, *i.e.* loss of CO with R + OH or ROH as co-products. The relative branching ratios for these three channels are given in Table 2. In comparing our quantitative findings with those of others, it is, of course, necessary to bear in mind the different experimental conditions, especially the photolysis wavelength(s). In other modern investigations,^{4,13,14,16} photodissociation has been initiated with a pulsed laser, usually at 193 nm, rather than a flashlamp which produces ultraviolet light over a range of wavelengths down to a limit determined by the transmission of Spectrosil quartz.

Within the wavelength range emitted by the flashlamp and transmitted by Spectrosil quartz, trifluoroacetic acid exhibits two absorption bands: a weak system ($\lambda_{\text{peak}} \sim 205$ nm; $\epsilon_{\text{peak}} \sim 45$ dm³ mol⁻¹ cm⁻¹) and a stronger system to shorter wavelengths ($\lambda_{\text{peak}} \sim 160$ nm; $\epsilon_{\text{peak}} \sim 2 \times 10^3$ dm³ mol⁻¹ cm⁻¹).²⁵ The former has been assigned²⁵ to a n- π^* transition on the carbonyl group; the latter to a n-3s Rydberg transition. The n- π^* band shows a little structure but the band at shorter wavelength is completely unstructured.

In acrylic acid, the weak n- π^* transition is shifted to longer wavelengths, starting at *ca.* 280 nm and merging into a stronger system below *ca.* 220 nm.¹⁵ This stronger band ($\lambda_{\text{peak}} \sim 185$ nm; $\epsilon_{\text{peak}} \sim 5.5 \times 10^3$ dm³ mol⁻¹ cm⁻¹) was originally assigned as a π - π^* transition within the vinyl group.¹⁵ However, based on a study of emission from acrylic acid excited at 199 nm, Arendt *et al.*²⁹ concluded that absorption of a photon in that region promotes an electron to a π^* orbital which is a mixture of π^* (C=C) and π^* (C=O) and that this state then predissociates. Others have shown that excitation of acrylic acid within this same band, but at 193 nm, gives rise to HOCO (among other photochemical products).^{2,4}

The ultraviolet light from the flashlamp used in our experiments would excite each acid in the two bands described in the previous paragraphs. The absolute yields of photochemical products were found not to vary linearly with the partial pressure of the acid, suggesting that at acid concentrations lower than those present in the current experiments, absorption in the lower wavelength system was probably predominant. At higher acid concentrations, significant excitation probably occurs in both absorption bands. We note that the

relative yields of HOCO, CO₂ and CO do not, within experimental error, depend on the concentrations of trifluoroacetic or acrylic acid through the ranges of partial pressure employed in these measurements.

As mentioned in the Introduction, the only paper on trifluoroacetic acid which seems relevant to the present study is that of Mearns and Back.¹² They photolysed relatively high partial pressures of the acid at temperatures between 90 and 190 °C using light between 200 and 220 nm. Perhaps their clearest and most valuable result was their observation among the products of C₂F₆, providing strong evidence for the formation of CF₃ radicals *via* steps (P.1), (P.2a) and (P.3a). No CF₃OH was reported and although CF₃H was detected it could have been formed indirectly, for example by reaction of CF₃ radicals with CF₃COOH.

On the basis that addition of isobutane reduced the yields of CO₂ and CO, Mearns and Back concluded that (P.1) was the main primary process in the photolysis of trifluoroacetic acid. However, we note that the yields of CO₂ and CO were only *reduced* by addition of isobutane, to apparently steady yields, and that the CO₂ : CO ratio at high concentrations of isobutane was the same as that which we determine directly, within experimental error. It seems likely that, in Mearns and Back's experiments in the absence of isobutane, radicals formed in the primary process could undergo reactions yielding certainly CO₂, *e.g.* CF₃ + CF₃COOH → CF₃ + CO₂ + CF₃H, and possibly CO. We agree with Mearns and Back that (P.1) is a major channel in the ultraviolet photolysis of CF₃COOH but not that it is *the* major channel.

Our results for acrylic acid are broadly in agreement with those of Rosenfeld and Weiner¹³ and of Lessard.¹⁴ Our data show strong evidence for the production of the vibrationally excited CO₂ which was observed by Rosenfeld and Weiner from its infrared fluorescence. They did not observe emission from CO, but it should be noted that the emission coefficient for the (1, 0) band of CO is *ca.* 14 times smaller than that for (00⁰1, 00⁰0) band of CO₂ so emission from vibrationally excited CO may have been below their detection limits. Lessard¹⁴ observed both CO₂ and CO by kinetic infrared absorption spectroscopy when acrylic acid was photolysed at 193 nm. He measured significant production of vibrationally excited species but made no attempt to quantify the product branching ratios.

It is harder to match our data with the measurements and interpretations of Miyoshi *et al.*⁴ and Kitchen *et al.*¹⁶ The latter group performed photofragment translational spectroscopy experiments on acrylic acid using an ArF excimer laser ($\lambda = 193$ nm) for photolysis and electron impact (200 eV) mass spectrometry to detect products. Their main observations, and certainly those of most relevance in a comparison with the present work, were made at mass-to-charge ratios of $m/e = 44$ and $m/e = 17$. Each distribution showed two peaks with maxima at essentially the same flight times for $m/e = 44$ and $m/e = 17$. On this basis, Kitchen *et al.* ascribed both peaks at each m/e to daughter ions of HOCO. To explain the difference in flight times, and the derived centre-of-mass product translational energy distributions, they invoked the production of an electronically excited state of HOCO at *ca.* 150 kJ mol⁻¹ excitation energy and they concluded that neither loss of CO₂

(decarboxylation) nor loss of CO (decarbonylation) is a significant primary photodissociation channel.

It is possible that the difference between the conclusion of Kitchen *et al.*¹⁶ that only primary C—C and C—O bond fissions are major pathways, and our own conclusion that photodissociation occurs at comparable rates *via* pathways (P.1), (P.2) and (P.3), is entirely due to differences in the experimental conditions, especially the photolysis wavelength. However, this seems unlikely and we have examined possible alternatives. First we note that the exothermicities of channels (P.1) and (P.3a) differ by 151 kJ mol⁻¹,³⁰ almost exactly the energy of the excited state of HOCO invoked by Kitchen *et al.*¹⁶ to explain the slower moving peaks in the time-of-flight mass spectra for $m/e = 17$ (and $m/e = 44$). Of course, the translational energy distribution of any OH formed in a process, like (P.3a), generating three fragments will depend on the details of the energy release but the energy difference between these pathways is, at least, highly suggestive.

Of course, channel (P.3) does not produce CO₂ and relatively slow moving species were also observed at $m/e = 44$ in the experiments of Kitchen *et al.*¹⁶ Our experiments indicate appreciable decarboxylation *via* channel (P.2) and it seems that the CO₂ produced in this channel might be responsible for the slower-moving species at $m/e = 44$, despite the fact that the exothermicity of (P.2a) is not a lot less than that of (P.1), if the light H atom were to carry off a major portion of the energy released in this process. For example, if process (P.2a) occurs by successive C—C and O—H bond breakages, much of the energy released as HOCO fragments to CO₂ + H must inevitably go into the motion of the H atom.³¹ Therefore we speculate whether the slower moving species observed at $m/e = 44$ in the experiments of Kitchen *et al.* could be CO₂ molecules created in channel (P.2a). What is certain is that further investigation of the photodissociation of carboxylic acids is required to pin down the primary processes occurring and whether these change with the wavelength of the photolysis source.

Miyoshi *et al.*⁴ compared the kinetic behaviour of HOCO radicals formed from photodissociation of acrylic acid at 193 nm with that of HOCO formed as a product of the almost thermonutral reaction between Cl atoms and formic acid. In the presence of any added reagent, loss was more rapid in the former case. Moreover, the loss did not obey first-order kinetics and it was faster at lower total pressures. Miyoshi *et al.*⁴ attributed this accelerated loss rate to dissociation of vibrationally excited HOCO radicals by tunnelling through the barrier separating HOCO from H + CO₂.⁷

Our observations show no evidence of formation of CO₂ from a slow, tunnelling, dissociation of HOCO. There is no change in the relative yields of CO₂ and HOCO when the total helium pressure is increased from 10 to 50 Torr (see Fig. 3) nor is there any slow rise in the CO₂ signal that can be ascribed to slow decomposition of HOCO. Moreover, we point out that in the experiments of Miyoshi *et al.*, vibrationally excited HOCO would have to survive something like 10⁵ collisions with H₂ for tunnelling to be responsible for the observed decay, since it takes place over several milliseconds. We point out that the secondary chemistry will be far more complex in the case where HOCO is produced from acrylic acid, rather than from the Cl + HCOOH reaction, since all three photochemical channels that we observe, and possibly other channels (see Table 1), generate radicals. The radicals will undoubtedly undergo secondary chemistry including pressure-dependent radical-radical reactions. It seems possible that some of this chemistry, which is not present in the case where HOCO radicals are produced from Cl + HCOOH, may be responsible for the removal of HOCO on long time-scales observed in the experiments of Miyoshi *et al.*

The present experiments clearly show that the ultraviolet photodissociation of trifluoroacetic and acrylic acids proceeds

Table 2 Branching ratios for different channels in the photodissociation of trifluoroacetic and acrylic acids

Products	R = CF ₃	R = CH ₂ =CH
RCOOH → R + HOCO	0.28 ± 0.07	0.32 ± 0.08
RCOOH → R + H + CO ₂	0.61 ± 0.09	0.37 ± 0.08
RCOOH → RH + CO ₂		
RCOOH → R + OH + CO	0.11 ± 0.06	0.31 ± 0.09
RCOOH → ROH + CO		

by at least three channels – those producing HOCO, CO₂ and CO. In the case of the decarboxylation and decarbonylation, our measurements provide no information as to whether the co-products are molecular (*i.e.*, RH and ROH) or two radicals (*i.e.*, R + H and R + OH). The experiments of Mearns and Back¹² on trifluoroacetic acid do, however, provide compelling evidence for a high yield of R = CF₃ in that case.

It is intriguing to speculate on whether the decarboxylation and decarbonylation of trifluoroacetic and acrylic acids occur simultaneously with, or sequentially to, the channel (P.1) which yields HOCO. It is possible that fission of the C–C bond generates a fraction of the HOCO with sufficient internal energy to undergo further decomposition. However, the high relative yields of both CO₂ and CO from acrylic acid, assuming the co-products to be C₂H₃ + H and C₂H₃ + OH suggest that this is unlikely since the exothermicity of channel (P.1) in this case (see Table 1) is only slightly greater than the thresholds for decomposition of HOCO to either H + CO₂ or OH + CO. Consequently, the HOCO formed in (P.1) would have to absorb essentially the whole of the exothermicity as internal energy if HOCO were to decompose and the likelihood that a large fraction of the HOCO radicals are formed within this range of internal energy seems small.

In conclusion, our results have confirmed the multichannel nature of the ultraviolet photodissociation of these two carboxylic acids and we have determined the relative yields in three of these channels. We believe that studies of these processes using pulsed lasers to produce and observe products could provide fascinating insights into the photodissociation dynamics of these species.

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