MULTIPHOTON GAS PHASE DISSOCIATION OF METHYL AND ETHYL FORMATES

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Summary

The IR-multiphoton-initiated decomposition of methyl and ethyl formates is reported. Experiments were carried out by 9.6 μm irradiation under mildly focused conditions, with fluences of about 10 J cm^{-2}. CO, CH_4, CO_2, C_2H_6 and CH_3OH were detected for $HCOOCH_3$ while CO, CH_4, C_2H_4, C_2H_2 and traces of CO_2 were observed for $HCOOC_2H_5$. The product yields were measured by quantitative gas chromatographic analyses. In $HCOOC_2H_5$, the dominant process is the reaction producing ethylene and CO (already observed in pyrolysis and UV photolysis). In $HCOOCH_3$ two presumably unimolecular reactions seem to occur, one producing CO and CH_3OH and the other producing CH_4 and CO_2, in contrast with the assumed mechanisms for pyrolysis and photolysis. The product yields can be interpreted in terms of secondary thermal or radical reactions. The effects of inert gases were studied. Luminescence in the focal region originating from OH·, CH·, C_2 and $H_2O(113)$ excited species was observed and its temporal behavior studied.

1. Introduction

The dissociation of large molecules in an intense IR field, as provided by high power pulsed CO_2 lasers, has led to the generation of a large number of papers in recent years [1]. At low pressures the interpretation of experimental data is relatively easy, because it is a well-established fact that the excitation in the quasicontinuum region is statistically distributed among all the vibrational manifolds of the molecules. Large molecules possess high densities of vibrational and rotational states and so one would expect a minimum of bottleneck effects in the pumping of high energy states. Moreover,

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theories like RRKM can be successfully applied to describe the intramolecular energy flow and unimolecular dissociation rates [2].

These same reactions, studied at higher pressures (collisional regime) are not so simple to understand. In fact, a rich gas phase chemistry arises from the primary dissociation products and this method has been applied as an interesting way of studying bimolecular reactions [3]. In fact, many times laser-initiated reactions show themselves to be only high temperature decompositions and much effort has been expended on the problem of distinguishing between thermal processes and truly laser-driven reactions [4].

In this paper we describe the multiphoton dissociation of methyl and ethyl formates. Both esters absorb electromagnetic radiation in the 1000 cm^{-1} region, owing to the C—O stretching vibrational mode, and we have been able to dissociate them with CO_2 laser radiation in both the 9.6 μm and the 10.6 μm regions.

The pyrolysis of alkyl formates containing a β-hydrogen in the alkyl group has been studied [5]. Decomposition products consist of formic acid and the corresponding olefin and the mechanism is believed to be a unimolecular reaction proceeding via a six-membered cyclic transition state. The interpretation of these results, however, is difficult, owing to the decomposition of formic acid into H_2, CO, CO_2, H_2CO and H_2O.

Ethyl formate thermal decomposition has been studied by Blades and Sandhu [6] in a toluene atmosphere in order to avoid radical reactions from HCOOH. The only products observed in these experiments were HCOOH and C_2H_4.

The pyrolysis of methyl formate was studied by Jain and Murwaha [7] in the range 476 - 500 °C. The products were H_2CO, CO, H_2 and traces of unidentified substances. It was observed that the initial process was the reaction

$$HCOOCH_3 \longrightarrow 2H_2CO$$

later observed by Krishnamachari [8] by flash photolysis. This was found to be a first-order process, probably proceeding via an intermediate state with a five-membered ring.

Ausloos has studied the photolysis of several alkyl formates [9]. The products of methyl formate (liquid phase) were CO, CH_4, H_2 and CO_2. In gaseous ethyl formate, the detected products were C_2H_4, C_2H_6, C_3H_8 and C_4H_{10}, suggesting the following primary processes:

$$\begin{aligned} HCOOR + h\nu &\longrightarrow HOR + CO \\ &\longrightarrow HCO\cdot + OR\cdot \\ &\longrightarrow H\cdot + COOR\cdot \\ &\longrightarrow HCOO\cdot + R\cdot \end{aligned}$$

For alkyl formates containing a β-hydrogen, the reaction producing HCOOH plus alkene was found also to occur.

The photolysis of methyl formate in the gas phase was studied by Yee and Thynne [10] in the range 30 - 103 °C, and H_2, CH_4, CO, CH_3OCH_3, H_2CO, C_2H_6, CO_2 and CH_3OH were detected as products. The following primary processes were proposed:

$$HCOOCH_3 + h\nu \longrightarrow CH_3OH + CO$$
$$\longrightarrow CH_4 + CO_2$$
$$\longrightarrow HCO\cdot + \cdot OCH_3$$
$$\longrightarrow HCOO\cdot + \cdot CH_3$$
$$\longrightarrow H\cdot + \cdot COOCH_3$$
$$\longrightarrow H\cdot + CO_2 + \cdot CH_3$$

The process was shown essentially to involve radicals, since upon NO addition no CH_4 was formed and the CH_3OH yield was reduced by 97%, thus showing that the first two reactions made a minimal contribution.

Krishnamachari [8] has studied the flash photolysis of methyl formate and found that methoxyl radicals are the most efficient precursors of formaldehyde with respect to the formyl radicals.

2. Experimental details

Methyl and ethyl formates were dissociated with a multimode tunable CO_2 TEA laser (Tachisto model 215 G), whose output wavelength was measured with an Optical Engineering (model 16A) spectrum analyzer, calibrated with an He–Ne laser. Pulse energies were monitored using a Coherent Radiation (model 210) pyroelectric power meter. The laser beam was focused by a ZnSe antireflection coated lens of focal length 25.4 cm and fluences were kept around 10 J cm^{-2}.

The photolysis cell was made of glass (length, 22 cm; inner diameter, 2 cm) and sealed on both sides with NaCl windows. The cell had a side compartment for holding the gas used as a chromatographic standard. The gas was allowed to enter the cell after the irradiation. All stopcocks were made of Teflon and the vacuum lines used for filling the cell and for introducing the irradiated samples into the gas chromatograph were made of metal and were free of grease. Pressures below 10.00 Torr were measured using a capacitance manometer (MKS Baratron model 221 A) and a Bourdon-type manometer was used for measuring higher pressures (Wallace and Tiernan, model 61C-ID).

Dissociation products were identified and quantitated using gas chromatography (CG model 20D), with a thermal conductivity detector, helium being the carrier gas, and with Porapak-S, Carbowax 20 M and Molecular Sieve 13-X columns. The sensitivity of the detector was calibrated using known quantities of an appropriate pure substance. The chromatographic

standards used were suited to the sample composition and the column used to carry out the quantitative analysis.

Methyl formate was from Riedel-de Haen (analytical grade) and ethyl formate from BDH (also analytical grade). The esters' purities were tested by gas chromatography and no detectable impurities were found in them. Gases were research grade (Matheson) and were used without purification.

The luminescence curves from excited reactive intermediates were observed through appropriate narrow bandpass interference filters (Oriel) using a fast photomultiplier (RCA, C31034A-02) and then displayed on a storage oscilloscope (Tektronix model 468).

Both esters were observed to obey the Beer–Lambert absorption law for laser light absorption up to 100 Torr pressure.

3. Results and discussion

3.1. End-product studies of methyl formate dissociation

Samples of methyl formate (initial pressure, 7.00 Torr) were irradiated with the P(20) line of the 00^01-02^00 band at 9.6 μm (1046.8 cm^{-1}). After 400 pulses, gas chromatography analysis showed CO, CH_4, CO_2, C_2H_6 and CH_3OH. Irradiation with the P(20) line of the 00^01-10^00 band at 10.6 μm (944.2 cm^{-1}) showed only CO, CH_4 and CO_2 in detectable quantities. Trace amounts of H_2 were also detected in both cases, but no attempt to quantitate this product was made, owing to uncertainties inherent to H_2 detection by thermal conductivity using helium as carrier gas [11]. All subsequent irradiations were carried out using the 1046.8 cm^{-1} CO_2 laser line, owing to the larger product yield and consequently smaller relative errors in the product analysis.

Quantitative analyses of dissociation products were carried out in a Porapak-S column at 35 °C (CO, CO_2, CH_4 and C_2H_6) using C_3H_6 as standard and Carbowax 20 M at 60 °C (CH_3OH) using diethyl ether as standard.

Table 1 shows the normalized partial pressures of dissociation products as a function of initial sample pressure. It is remarkable that the observed yields for CO, CO_2 and CH_3OH (within the experimental error) are constant and independent of sample pressure. This may possibly be evidence for the occurrence of the following processes:

$$HCOOCH_3 + nh\nu \longrightarrow CO + CH_3OH \quad (I)$$

$$\longrightarrow CH_4 + CO_2 \quad (II)$$

The presence of C_2H_6 among the products is evidence of C—O bond breakage with the formation of $CH_3\cdot$ radicals, which can either abstract a hydrogen atom to form CH_4 or combine with another $\cdot CH_3$ to form C_2H_6. This last process is predictable, considering the small volume of the focal region and therefore high local radical concentration. The following free radical reactions take place:

TABLE 1

Normalized pressures of dissociation products of methyl formate (400 pulses, 0.8 J per pulse)

P_i (Torr)	P(products)/P_i(ester)				
	CO	CH_4	CO_2	C_2H_6	CH_3OH
0.50	0.199 ± 0.001	—	—	—	—
2.00	0.200 ± 0.002	0.015 ± 0.001	0.010 ± 0.002	0.009 ± 0.001	0.078 ± 0.002
4.00	0.199 ± 0.001	0.012 ± 0.002	0.010 ± 0.001	0.008 ± 0.001	0.078 ± 0.001
6.00	0.197 ± 0.001	0.013 ± 0.001	0.010 ± 0.001	0.006 ± 0.002	0.075 ± 0.002
8.00	0.198 ± 0.001	0.013 ± 0.001	0.010 ± 0.001	0.007 ± 0.001	0.078 ± 0.002
10.00	0.195 ± 0.002	0.012 ± 0.001	0.011 ± 0.001	0.004 ± 0.002	0.075 ± 0.001

Each displayed numeral is the mean value for ten experiments. Errors are standard deviations for each case.

$$HCOOCH_3 + nh\nu \longrightarrow HCOO\cdot + CH_3\cdot \qquad \text{(III)}$$

$$\text{CO, } CO_2\text{, } H_2O\text{, } H_2 \qquad CH_4\text{, } C_2H_6$$

Although water could not be detected among the reaction products, its formation cannot be discarded. Our cell is made of glass and therefore water can easily remain adsorbed on the walls, and stay undetected if it is formed in small enough quantities. The fact that methane may be formed in the processes following reaction (III) may explain the non-stoichiometric relationship between the yields of CH_4 and CO_2. It is also noteworthy that in the focal region of the laser beam CH_3OH may undergo multiphoton dissociation [12]; this could account for the non-stoichiometric relation between the yields of CO and CH_3OH.

Table 2 shows the effects of adding helium and argon to the ester. It is apparent that helium causes a definite lowering of the product yields. This can be explained by the high efficiency of this gas in the deactivation of excited species. Since chemical processes following the laser pulse are controlled by hydrodynamic gas flow, energy transfer and thermal conductivity [13], it is reasonable to assume that the efficiency of helium in decreasing the product yields is related to a hydrodynamic effect (*i.e.* fast expansion) leading to an effective reduction in temperature at the focal region, as observed by Braun *et al.* for the case of acetone [14].

Argon, however, can increase or lower the product yields. In this case we must consider two possible modes of behavior: the argon may act as a thermal bath and therefore transfer energy to molecules which can dissociate (rotational hole filling), or it may act as a deactivator of vibrationally excited molecules. In the case of helium, the second process dominates owing to the high velocity of the helium atoms. Considering argon, both processes occur to comparable extents and obviously at higher pressures deactivation predominates. This explains the fact that at low argon pressures the yields

TABLE 2

Product yields of $HCOOCH_3$–He and $HCOOCH_3$–Ar mixtures

P_{He} (Torr)	10^3P(products)/P_i(ester)		
	CO	CO_2	CH_4
0	69 ± 1	5.4 ± 0.2	3.1 ± 0.3
1.00	70 ± 2	5.9 ± 0.3	3.8 ± 0.2
3.00	62 ± 3	4.7 ± 0.1	3.1 ± 0.3
5.00	50 ± 2	4.2 ± 0.3	2.4 ± 0.1
7.00	51 ± 2	3.6 ± 0.1	2.1 ± 0.2
9.00	43 ± 1	3.4 ± 0.1	1.8 ± 0.1
P_{Ar} (Torr)	10^3P(products)/P_i(ester)		
	CO_2	CH_4	C_2H_6
0	5.4 ± 0.2	3.1 ± 0.3	2.0 ± 0.1
1.00	6.2 ± 0.3	4.2 ± 0.2	2.5 ± 0.4
3.0	7.6 ± 0.2	5.2 ± 0.3	2.6 ± 0.3
6.0	9.7 ± 0.3	7.6 ± 0.3	3.1 ± 0.2
8.0	8.8 ± 0.3	8.0 ± 0.2	2.4 ± 0.1
10.0	6.0 ± 0.2	7.8 ± 0.3	1.9 ± 0.2
12.0	5.5 ± 0.2	7.8 ± 0.2	1.5 ± 0.2

400 pulses, 0.5 J per pulse. Initial ester pressure, 9.00 Torr.

increase with increasing pressure but fall at high pressures, as can be seen in Table 2.

In an attempt to clarify this problem we monitored the CO yields (the largest and the easiest to analyze with minimum errors) as a function of added gases, inert or otherwise. These samples were analyzed in a molecular sieve 13-X column at 25 °C; the added gas itself was used as the chromatographic standard. Table 3 summarizes these results.

TABLE 3

CO yield in $HCOOCH_3$ mixtures

P_{gas} (Torr)	$10^2P_{CO}/P_i$(ester)				
	H_2	*Ar*	*Ne*	*NO*	O_2
0	5.2 ± 0.1	5.2 ± 0.2	4.9 ± 0.1	5.2 ± 0.3	5.1 ± 0.2
5.00	4.8 ± 0.1	7.5 ± 0.2	5.1 ± 0.2	5.1 ± 0.4	5.0 ± 0.2
10.0	3.9 ± 0.2	8.0 ± 0.2	6.9 ± 0.3	5.2 ± 0.3	5.0 ± 0.2
15.0	2.9 ± 0.1	8.7 ± 0.2	6.6 ± 0.1	5.2 ± 0.3	5.7 ± 0.3
20.0	—	7.4 ± 0.2	6.3 ± 0.5	5.2 ± 0.1	8.4 ± 0.4
25.0	—	—	—	4.7 ± 0.2	5.8 ± 0.4

400 pulses, 0.5 J per pulse. Initial ester pressure, 5.00 Torr.

It is noticeable at first sight that all the gases behave similarly, except for hydrogen which consistently lowers the CO yield as a function of pressure. The explanations already presented in the comparison between helium and argon still hold. A striking fact is that even "reactive" gases, such as H_2 and O_2, and NO which is a very well-known free-radical scavenger, behave similarly to the inert gases. In each case no new substances could be detected. This is not in itself evidence, because NO can react without the appearance of new products [14]. This behavior has been observed in other systems under multiphoton dissociation in a focused geometry [16] and is probably due to the very small volume of the focal region, where radicals are present in a high local concentration. Under these conditions radical–radical reactions may easily occur, since they have activation energies close to zero [17].

An entirely different phenomenon occurred when methyl formate (10.00 Torr) was mixed with excess O_2 (40.00 Torr). The first laser pulse caused an explosion with a luminescence in the whole cell. The only products detected were CO_2 (Porapak S), water (Carbowax 20 M) and traces of CO (MS 13-X); the ester disappeared completely. Here, the process is completely different from the preceding ones, since the reaction is probably initiated by dielectric breakdown [18].

It is also interesting to point out that no reaction at all was observed for any system at any wavelength when the 25.4 mm focal length lens was substituted by a 1 m focal length gold-coated copper mirror. This result indicates the importance of power density in this case, where the absorption coefficient is really low.

3.2. End-product studies of ethyl formate dissociation

Irradiation of 10.0 Torr samples of ethyl formate showed CO, CH_4, CO_2 (in trace amounts), C_2H_4 and C_2H_2 when the laser was tuned to the P(20) line of the 9.6 μm band. Irradiation at P(20) of the 10.6 μm band under the same experimental conditions showed only C_2H_4 and CO in trace amounts. At 9.6 μm C_2H_4 and CO are the dominant products, as is shown in Table 4, where the study of product yields as a function of the initial ester pressure is summarized.

The $(C_2H_4 + C_2H_2)$ normalized yield remains constant (within our experimental error limits) through the whole pressure range studied. This may mean that ethylene is formed via a unimolecular process followed by thermal decomposition to give acetylene (the local temperature at the focal point is known to be high):

$$HCOOC_2H_5 + nh\nu \longrightarrow CO + H_2O + C_2H_4 \quad \text{(IV)}$$

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \quad \text{(V)}$$

Thermal decomposition of ethylene is a very well-known high temperature reaction [16].

Water was not detected, possibly for the same reason as that discussed for methyl formate. Methane is often a product of radical reactions; in this

TABLE 4

Normalized pressures of dissociation products of $HCOOC_2H_5$ (400 pulses, 0.8 J per pulse)

P_i (Torr)	P(products)/P_i(ester)				
	CO	CH_4	C_2H_4	C_2H_2	$C_2H_4 + C_2H_2$
2.00	0.359 ± 0.005	—	0.383 ± 0.004	0.018 ± 0.003	0.401 ± 0.002
4.00	0.344 ± 0.005	0.011 ± 0.001	0.376 ± 0.002	0.043 ± 0.001	0.419 ± 0.002
6.00	0.330 ± 0.001	0.017 ± 0.001	0.348 ± 0.001	0.060 ± 0.001	0.408 ± 0.001
8.00	0.324 ± 0.003	0.017 ± 0.001	0.326 ± 0.003	0.071 ± 0.002	0.398 ± 0.003
10.00	0.323 ± 0.004	0.019 ± 0.001	0.319 ± 0.004	0.083 ± 0.001	0.402 ± 0.004

case it may be formed in the breakage of the ester C—O bond of the ethyl formate molecule:

$$HCOOC_2H_5 + nh\nu \longrightarrow HCO\cdot + \cdot OC_2H_5 \qquad \text{(VIa)}$$

$$\cdot OC_2H_5 \longrightarrow CH_4 + CHO\cdot$$

Fission of the C—C bond of the ethyl group or the alcoholic C—O bond is unlikely, since no C_2H_6 was found among the products, even in trace amounts.

Another possible secondary reaction (considering the initial energy from the irradiation) could be

$$\cdot OC_2H_5 \longrightarrow \cdot OH + C_2H_4 \qquad \text{(VIb)}$$

whose occurrence might be supported by the observation of emission from OH· radicals. This observation, of course, does not support fully the occurrence of reaction (VI), since OH· can come from many processes under our experimental conditions. The existence of OH· radicals can account for the consumption of CO through the reaction

$$OH\cdot + CO \longrightarrow CO_2 + H \qquad \text{(VII)}$$

Literature data [17] for reaction (VII) are $\Delta H^\circ = -24.4$ kcal mol^{-1} and $k = 3.1 \times 10^{11} \exp(-600/RT)$. This is a really low activation energy process and it may account for CO consumption (non-stoichiometry with relation to C_2H_4) and the appearance of CO_2 in trace quantities. Unfortunately as the quantities were so low we were unable to make a proper quantitative analysis for this product. It is also necessary to consider the possibility of direct formation of CO_2:

$$HCOOC_2H_5 + nh\nu \longrightarrow CO_2 + H_2 + C_2H_4 \qquad \text{(VIII)}$$

despite the fact that its ΔH° is greater than that of reaction (IV). As the activation energies for these processes are not known this problem remains open.

In an attempt to study the efficiency per pulse for this dissociation we have measured product yields as a function of the number of pulses per irradiation. Unfortunately linear or logarithmic plots do not show any clear trend.

Anyway, the constancy of C_2H_4 and CO yields with pressure suggests that the olefin elimination is a unimolecular reaction, as observed in early studies of pyrolysis and photolysis of this ester [5, 9]. This is a far easier pathway (lower activation energy) for the ester decomposition than the complicated rearrangements necessary for the $HCOOCH_3$ decomposition; this is reflected in the efficiency of product formation in each case as can be seen in Tables 1 and 4.

3.3. Observations of excited intermediates

When irradiating the ester samples, a weak luminescence can be seen in the focal region. Using interference filters we were able to isolate emissions at 310, 430, 515 and 633 nm. These emissions are the same for both esters and can be assigned to well-known transitions of OH· radicals (310), CH· (430), C_2 molecule (515) and H_2O $113 \rightarrow 000$ transition (633 nm). These are bands already observed in flames [19] and in multiphoton dissociation processes [12, 20, 21]. Using temporal resolution, we observed the emission curves for these transitions. These curves were reproduced by computer simulation using a sum of two exponentials, one of which (the rise time) was the reciprocal of the radiative lifetime for the species and transition considered. The decay is the formation rate for the corresponding excited species [20]. Calculated values are shown in Table 5.

The calculated values for radiative lifetimes agree, within our experimental error, with the values reported in the literature [22]. The nature of the species and chemical reactions which yield this behavior are, however, less clear. The presence of CH· and C_2 in combustion-type reactions is very

TABLE 5

Calculated rate constants for excited intermediate fluorescence: k_1 (formation) and k_2 (decay) (all values are in reciprocal seconds)

Ester	*310 nm*		*430 nm*		*515 nm*		*633 nm*	
	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
$HCOOCH_3$, P = 10.00 Torr	2×10^6	4×10^5	2×10^7	2×10^6	3×10^6	4×10^5	1×10^6	3×10^6
$HCOOC_2H_5$, P = 9.50 Torr	4×10^6	5×10^5	3×10^7	2×10^6	4×10^6	6×10^5	1×10^6	3×10^6

common, although their origin is not clear. In the present case we believe that they may arise from the initial photofragments by dissociation, owing to the high temperature in the focal region:

$$\text{Photofragment} \xrightarrow{k_1} A^* \xrightarrow{k_2} A$$

The temperature effect is substantiated by the increasing production of C_2H_2 in the ethyl formate decomposition. This is a very well-known high temperature process and has been observed under similar conditions [16].

The rise and decay constants were the same (within our experimental error, about 20%) when the esters' pressures were lowered to 5.00 Torr. They were also insensitive to argon addition (5 Torr). This may be evidence of excited intermediate formation through decomposition of photofragments, since the curve shape is insensitive to pressure changes. The water ($113 \rightarrow 000$) emission shows the same rise and decay constants as were observed in the case of ethanol [21], suggesting a similar process of formation.

4. Conclusions

The use of intense IR radiation to dissociate methyl and ethyl formates via multiphoton absorption shows that more than one reactive channel is responsible for the product distributions.

In the case of ethyl formate reaction (IV) is the most likely process. The main difference between multiphoton dissociation and UV photolysis [9] is the complete absence, in our case, of C_2H_6, C_3H_6 and C_4H_{10}, suggesting that radicals play a far less important role in MPD. This may, however, reflect the fact that the reaction volume (focal region) is very small and radical–radical reactions are favored. As in other cases, reaction (IV) seems to be a unimolecular process.

In contrast, for methyl formate the products are different from those of UV photolysis, namely the absence of formaldehyde, acetaldehyde and dimethyl ether in the present multiphoton dissociation studies. In contrast with ref. 10, reactions (I) and (II) seem to be the dominant processes. Reaction (III) is important here as well as in the cited studies. More dramatic contrasts arise when one compares MPD with pyrolysis [7]. The complete absence of H_2CO shows that under our experimental conditions an entirely different process (probably non-collisional) occurs. As H_2CO was also observed in the UV photolysis [8, 10] as a labile product we may possibly have a true MPD process, despite the fact that H_2CO could easily decompose under our experimental conditions. This problem could be clarified easily by a molecular beam experiment, where collisionless conditions can be obtained.

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