THE PHOTO-OXIDATION OF PROPIONALDEHYDE

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Summary

C_2H_5CHO vapor was photolyzed with 313 nm radiation at 22 °C in the presence of O_2 and O_2–He, O_2–N_2, O_2–NO and O_2–*cis*-2-C_4H_8 mixtures. The contents of the reaction mixture were allowed to bleed through a pinhole into a quadrupole mass spectrometer providing for continuous monitoring of the C_2H_5OH and $C_2H_5C(O)O_2H$ produced. CO, CO_2, C_2H_4 and CH_3CHO concentrations were determined by gas chromatography. From CO quantum yield determinations we found that the only photolytic process of importance is the following:

$$C_2H_5CHO + h\nu \text{ (313 nm)} \xrightarrow{O_2} C_2H_5 + CO + HO_2$$
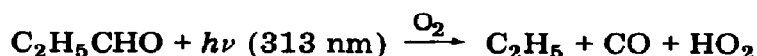
The CO quantum yields also indicate that the reactive state of C_2H_5CHO is pressure quenched, and the half-quenching pressures for the various reactant gases were measured. The primary quantum yield in 1 atm of air is 0.30 ± 0.05. The data suggest that the reacting state is a vibrationally excited triplet state which consists of levels which are quenched with different efficiencies by any quenching gas. The more rapidly quenched levels account for about 40% of the total, while the less rapidly quenched levels account for about 60% of the total. Large quantum yields were measured for CO_2, C_2H_5OH and $C_2H_5C(O)O_2H$ indicating a chain reaction initiated by abstraction of the aldehydic hydrogen of C_2H_5CHO by C_2H_5O radicals. The C_2H_4 quantum yields are dependent on the total pressure, and we believe that C_2H_4 is produced from the decomposition of vibrationally excited $C_2H_5CO_3$ radicals:

$$C_2H_5CO_3{}^* \rightarrow C_2H_4 + CO_2 + OH$$
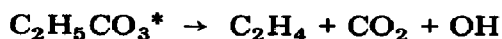
The deactivated $C_2H_5CO_3$ radicals will either react with HO_2 or C_2H_5CHO or at the walls to produce $C_2H_5CO_3H$, or ultimately decompose to $CO_2 + C_2H_5$. We found that the following reactions are unimportant at 22 °C:

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$$

$$HO_2 + C_2H_5CHO \rightarrow \text{adduct}$$
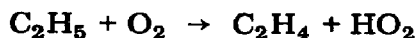
1. Introduction

The lower molecular weight aliphatic aldehydes are intimately involved in the chemistry of the photochemical smog process because of their high photochemical reactivity and the fact that they are initial products in the photo-oxidation of hydrocarbons [1]. Therefore a knowledge of the mechanism of the photo-oxidation of these aldehydes, of the relative rates of the free-radical reactions involved and of the fate of the aldehydes under atmospheric conditions is essential for the purposes of atmospheric modeling. The photochemistry of acetaldehyde and formaldehyde has been extensively studied [1 - 6]. There have been few detailed studies, however, of the photo-oxidations of higher aldehydes. McDowell and Sharples [7] studied the photo-oxidation of propionaldehyde at 313 nm and found perpropionic acid to be the principal product at relatively large propionaldehyde pressures, with a quantum yield of the order of 50. Altshuller *et al.* [8] studied propionaldehyde photo-oxidation at much lower aldehyde pressures where the chain length is small and found ethyl hydroperoxide to be a major product. They also found acetaldehyde and ethanol to be present but concluded that they were produced via a decomposition of the ethyl hydroperoxide during the analysis. A smog chamber study of propionaldehyde in the presence of nitrogen oxides has been done by Kopczynski *et al.* [1]. Their work demonstrates the high reactivity of propionaldehyde, compared with its lower molecular weight analogs, with regard to oxidant yields.

In all these studies the mechanisms were still somewhat speculative regarding the nature of the intermediates involved, and no adequate explanation was provided for the relatively high reactivity of propionaldehyde. The purpose of this work, then, was to make a systematic study of the photo-oxidation of propionaldehyde as a function of a wide variety of reactant conditions. We paid particular attention to determining the photolysis yields as a function of reactant conditions in order to provide insight into the nature of the primary process.

The photolysis of propionaldehyde at 313 nm has been studied by Blacet and Pitts [9] who found that the predominant primary process is

$$C_2H_5CHO + h\nu \ (313 \text{ nm}) \rightarrow C_2H_5 + HCO \tag{1}$$
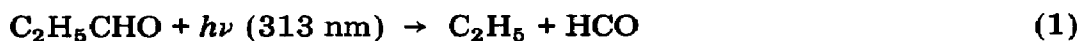
The absorption produces a vibrationally excited singlet state intermediate [10]. In the presence of O_2, formyl radicals react solely via

$$HCO + O_2 \rightarrow CO + HO_2 \tag{2}$$

to produce CO [5, 11]. Therefore, measurement of the CO quantum yields provides a direct measure of the quantum yield for process (1).

It was also our goal to determine the ultimate fate of the peroxypropionyl radical under the conditions of our experiments.

2. Experimental details

The photolysis of propionaldehyde vapor was performed in a 500 cm^3 Pyrex bulb by irradiation from a Hanovia medium pressure mercury lamp. The 313 nm line was isolated with a Corion SM-3130-2 interference filter. All experiments were carried out at 23 ± 1 °C. Gases were admitted to the reaction cell through a conventional grease-free vacuum line. The contents of the reaction cell were allowed to bleed continuously through a small pinhole into an Extranuclear type II quadrupole mass spectrometer providing for continuous product analysis. Mass spectrometry determinations were performed by measuring product ion current peaks relative to the $m/e = 84$ peak from a small amount of krypton which was added to the reaction mixture before irradiation. The krypton pressure was measured with a McLeod gauge.

The CO, CO_2, C_2H_4, CH_3CHO and C_2H_5OH produced were all determined by expansion to a gas chromatograph sample loop after irradiation. All but CO were then separated on a stainless steel column 6 ft long with an outside diameter of 0.25 in packed with Porapak QS and operated at 130 °C with a helium flow rate of 40 cm^3 min^{-1}. C_2H_5OH was also determined by mass spectrometry in several experiments; however, the analysis was more difficult. CO was separated from O_2 and krypton on a stainless steel column 7 ft long with an outside diameter of 0.25 in packed with molecular sieve 5A. Propionic acid was calibrated and determined by measuring the relative signals of the $m/e = 74$ and the $m/e = 84$ peaks of krypton.

Propionaldehyde, obtained from Aldrich, was purified by trap-to-trap distillation from −63 to −161 °C. Matheson extra dry grade O_2 was used. CO_2 present as an impurity was removed by passing the O_2 through a trap cooled to −161 °C. Matheson chemically pure NO was used and distilled trap to trap from −184 to −196 °C. The krypton, helium, N_2, CO, CO_2 and C_2H_4 were Matheson research grade, high purity grade, prepurified grade, chemically pure grade, bone dry grade and chemically pure grade respectively. The cis-2-C_4H_8 used was Matheson technical grade and was distilled trap to trap from −94 to −161 °C. CH_3CHO, obtained from Aldrich, was distilled from −63 to −131 °C. Absolute C_2H_5OH was used without purification. The C_2H_5COOH used was Mallinckrodt analytical reagent grade.

Mass spectra of all gases were obtained and compared with the EPA–NIH Mass Spectral Data Base. In all cases no extraneous peaks were present.

Actinometry was performed by photolysis of azomethane and subsequent measurement of the N_2 produced by gas chromatographic separation on the molecular sieve column described earlier. The pressure of azomethane used was determined by matching absorbances with the pressure of propionaldehyde used in each experiment. The azomethane was prepared using a modified procedure reported by Renaud and Leitch [12]. It was purified by trap-to-trap distillation from −89 to −161 °C.

IR experiments were carried out in a long path IR cell vertically mounted in a Beckman model 10 IR spectrophotometer. In these experi-

ments the 313 nm line of the mercury lamp was isolated as in the mass spectrometry experiments.

3. Results

The photolysis of C_2H_5CHO in the presence of O_2 at 313 nm and 23 °C leads to the production of CO, CO_2, C_2H_4, CH_3CHO, C_2H_5OH and $C_2H_5C(O)O_2H$. We looked for, but could not find, mass spectral peaks corresponding to C_2H_5OOH or $(C_2H_5O)_2$. We expected the last two compounds to be formed, but they are not major products and probably are produced in amounts too small for us to detect mass spectrometrically.

The CO, CO_2, C_2H_4, CH_3CHO and C_2H_5OH were identified by their gas chromatographic retention time. CO_2, C_2H_5OH and CH_3CHO could also be seen mass spectrometrically. The $C_2H_5CO_3H$ was identified and monitored from the mass spectral peak at $m/e = 74$ which corresponds to $C_2H_5CO_2H$. However, this peak can be positively identified as originating from $C_2H_5CO_3H$ by two experiments described below which also show that no $C_2H_5CO_2H$ is produced as an initial product. The fact that no parent mass spectral peak appears for $C_2H_5CO_3H$ and only a peak corresponding to the mass of $C_2H_5CO_2H$ is exactly analogous to the situation for CH_3CO_3H [2]. It was assumed for calibration purposes that all the $C_2H_5CO_3H$ was converted to $C_2H_5CO_2H$ before mass spectral analysis.

Since $C_2H_5CO_3H$ is expected to come from the precursor radical $C_2H_5CO_3$, experiments were done with NO added which converts this radical to $C_2H_5CO_2$:

$$C_2H_5C(O)O_2 + NO \rightarrow C_2H_5CO_2 + NO_2$$
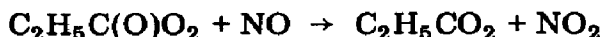
The addition of NO completely suppressed the formation of the mass spectral peak at $m/e = 74$. This cannot be attributed to the scavenging of $C_2H_5CO_2$ by NO, since the CO_2 yields were unaffected by NO addition. (The CO_2 comes from decomposition of $C_2H_5CO_2$.)

The second experiment to identify the product was done in a long path IR cell with 6.4 Torr of C_2H_5CHO and 6.6 Torr of O_2; the absorbed intensity I_a was about 5.4×10^9 photons cm^{-3} s^{-1}. During photolysis for 5 h the IR bands of $C_2H_5CO_3H$ at 1180 and 3280 cm^{-1} were observed. The mixture was then allowed to remain in the dark for 2.75 h. The $C_2H_5CO_3H$ bands became weaker, while the $C_2H_5CO_2H$ band at 3600 cm^{-1} grew, as also did the 2330 cm^{-1} band of CO_2 which is a decomposition product of $C_2H_5CO_3H$ [13].

Product quantum yields are given in Tables 1 and 2. The quantum yields $\Phi(CO)$ of CO decrease with increasing pressure of either C_2H_5CHO or O_2 from a value of about 1.0 at low pressures to values of about 0.2 at high pressures. For the C_2H_5CHO variation, it is difficult to see whether a limiting lower value for $\Phi(CO)$ is reached because the experiments are limited by the vapor pressure of C_2H_5CHO. However, with increasing O_2 pressure, a lower limiting value of $\Phi(CO) = 0.3 \pm 0.1$ is reached.

TABLE 1

Effect of C_2H_5CHO pressure on the photo-oxidation of $C_2H_5CHO^a$

[P] (Torr)	Irradiation time (min)	I_a (×10^12 photons cm^-3 s^-1)	$\Phi(CO)$	$\Phi(CO_2)$	$\Phi(C_2H_4)$	$\Phi(CH_3CHO)$	$\Phi(C_2H_5OH)$	$\Phi(C_2H_5CO_3H)$	I	$\dfrac{\Phi(CH_3CHO)}{\Phi(CO)}$
$[O_2] = 3.2 \pm 0.2$ Torr										
3.3	205	0.15	0.94	1.24	0.40	0.36	0.71	1.86	1.48	0.39
11.3	105	0.43	0.96	2.65	0.47	0.54	1.66	4.88	1.35	0.56
24.1	43	0.87	0.95	3.48	0.43	0.73	2.83	13.2	1.11	0.77
45.7	15	1.46	0.85	4.27	0.31	0.78	2.71	19.5	1.35	0.91
68.5	22	1.89	0.78	3.86	0.26	0.61	1.98	24.9	1.63	0.78
94.3	9.5	2.45	0.73	4.43	0.24	0.67	2.25	31.0	1.64	0.91
121	18	2.83	0.87	2.63	0.12	0.39	1.71	19.7	1.58	0.44
120	5	2.82	0.57	3.95	—	0.71	1.84	—	1.69	1.23
$[O_2] = 480 \pm 1$ Torr										
3.29	120	0.22	0.35	0.074	—	0.35	<0.05	<0.1	1.21	1.00
4.41	120	0.26	0.45	0.190	—	0.42	<0.05	<0.1	1.52	0.93
6.57	120	0.38	0.38	0.22	—	0.43	<0.05	<0.1	1.40	1.13
10.26	120	0.62	0.42	0.24	—	0.41	<0.05	0.41	1.61	0.98
$[O_2] = 500 \pm 3$ Torr										
1.02	480	0.066	0.28	0.039	—	0.26	<0.02	<0.2	1.23	0.93
2.04	300	0.13	0.26	0.081	—	0.24	0.086	<0.3	1.05	0.92
3.05	180	0.20	0.26	0.089	—	0.32	0.167	0.40	0.72	1.23
4.21	180	0.27	0.33	0.110	—	0.26	0.106	0.40	1.03	0.78
5.18	180	0.33	0.27	0.130	—	0.25	0.27	0.60	0.77	0.93

[a] P represents propionaldehyde in this and the following tables.

TABLE 2

Effect of O_2 pressure on the photo-oxidation of C_2H_5CHO at 10.7 ± 0.6 Torr of C_2H_5CHO[a]

$[O_2]$ (Torr)	Irradiation time (min)	$\Phi(CO)$	$\Phi(CO_2)$	$\Phi(C_2H_4)$	$\Phi(CH_3CHO)$	$\Phi(C_2H_5OH)$	$\Phi(C_2H_5CO_3H)$	I	$\dfrac{\Phi(CH_3CHO)}{\Phi(CO)}$
5.5	50	0.92	1.92	0.250	0.75	1.16	9.94	1.31	0.81
21.0	90	0.74	1.39	0.154	0.64	1.18	5.61	1.08	0.86
52.5	180	0.59	0.80	0.070	0.54	0.59	6.86	1.16	0.91
128	210	0.48	0.43	0.026	0.50	0.34	1.22	1.05	1.03
196	270	0.46	0.40	—	0.43	0.25	2.69	1.24	0.92
346	270	0.35	0.208	—	0.35	0.22	1.05	0.97	1.01
501	360	0.37	0.225	—	0.34	0.160	0.80	1.20	0.90
622	360	0.32	0.159	—	0.29	0.148	0.49	1.10	0.90
773	420	0.25	0.157	—	0.27	0.137	0.051	1.00	1.07

[a] $I_a = 4.7 \times 10^{10}[P]$ photons cm^{-3} s^{-1} for $[P]$ in torr.

TABLE 3

Effect of radiation time on the photo-oxidation of C_2H_5CHO[a]

$[P]$ (Torr)	$[O_2]$ (Torr)	Irradiation time (min)	$\Phi(CO)$	$\Phi(CO_2)$	$\Phi(C_2H_4)$	$\Phi(CH_3CHO)$	$\Phi(C_2H_5OH)$	$\Phi(C_2H_5CO_3H)$	I	$\dfrac{\Phi(CH_3CHO)}{\Phi(CO)}$
2.07	2.73	45	1.07	1.99	0.78	0.94	—	—	—	0.88
2.10	2.74	60	1.07	1.65	0.62	—	—	0.12	—	—
2.13	2.57	90	1.12	1.82	0.61	0.73	—	—	—	0.65
2.09	2.51	121	1.16	2.37	0.76	0.79	<0.70	—	>1.57	0.68
2.12	2.49	180	1.22	1.85	0.63	0.75	0.69	—	1.48	0.61

[a] $I_a = 1.26 \times 10^{11}$ photons cm^{-3} s^{-1}.

The difficulty experienced in attempts to achieve reproducibility of results has raised the possibility of secondary decay reactions, one of which has been previously alluded to in the case of $C_2H_5CO_3H$. Evidence of secondary decay comes from comparison of some of the product yields. From mechanistic considerations (see Section 4) it is expected that the products from the carbonyl end of C_2H_5CHO should equal the products from the C_2H_5 end, *i.e.*

$$I \equiv \frac{\Phi(CO) + \Phi(CO_2)}{\Phi(CH_3CHO) + \Phi(C_2H_5OH)} = 1.0$$

The values for I are listed in Tables 1 and 2, and in a few cases they greatly exceed 1.0 suggesting that CH_3CHO and C_2H_5OH have been further oxidized. It is also possible that the secondary decay of $C_2H_5CO_3H$ which produces CO_2 does not yield C_2H_5OH or CH_3CHO, resulting in elevated values for I. Gas chromatographic analysis of reacted mixtures which were allowed to remain in the dark for extended periods of time indicated excess CO_2 production. It is also apparent that the extent of secondary CO production may be a function of the chain length as can be seen from the large time dependence of CO formation in the two experiments performed at 120 Torr of C_2H_5CHO. From the observed decomposition of $C_2H_5CO_3H$ to CO_2 in the IR experiment and the fact that the mass balance excess always lies on the CO and CO_2 side it is clear that the discrepancy is not the result of analysis error.

To test for secondary decomposition, a series of runs was done for various reaction times. These results are given in Table 3. For small reaction times $\Phi(CO)$ approaches 1.0, but it increases as the irradiation time is lengthened. The results of these experiments and the two experiments in Table 1 at 120 Torr of C_2H_5CHO indicate that it is probably CH_3CHO which is contributing to secondary CO formation. Thus the secondary decay will complicate an interpretation of the data. Therefore all runs were done for as short a reaction time as practical. The reported values of I are an indication of the extent of any secondary decay.

The quantum yields of CO_2, C_2H_5OH and $C_2H_5CO_3H$ often exceed 1.0 indicating that the compounds are produced in a chain process. Reproducibility of these yields in different runs was not as good as for CO. This indicates that radical termination may occur on the reaction vessel walls, and the quantum yields of the chain products will be sensitive to wall conditions. This was confirmed by conditioning the cell walls with HI, I_2 and C_2H_5I over a period of a few weeks. Runs done after this conditioning showed markedly reduced quantum yields for CO_2 and $C_2H_5CO_3H$ but $\Phi(CO)$ was unaffected (data not given). This indicates that the $C_2H_5CO_3$ radical is terminated at the wall.

Experiments with air added were done (before the walls were conditioned with I_2) and the results are listed in Table 4. Added air reduces the product yields, and $\Phi(CO) \approx 0.34$ at the highest air pressure (588 Torr). Whether or not this is a limiting value is difficult to tell from the data.

TABLE 4

Photo-oxidation of C_2H_5CHO in air[a]

[P] (Torr)	[air] (Torr)	Irradiation time (min)	$\Phi(CO)$	$\Phi(CO_2)$	$\Phi(C_2H_4)$	$\Phi(CH_3CHO)$	$\Phi(C_2H_5OH)$	$\Phi(C_2H_5CO_3H)$	I	$\dfrac{\Phi(CH_3CHO)}{\Phi(CO)}$
6.84	4.54	75	1.09	3.56	0.56	0.65	2.55	4.00	1.24	0.60
7.06	10.8	75	0.95	3.41	0.45	0.61	2.04	2.47	1.41	0.64
7.25	20.8	75	1.03	3.01	0.22	0.57	1.97	2.47	1.46	0.55
7.04	43.1	75	0.92	2.34	0.127	0.51	1.62	1.75	1.44	0.55
7.28	82.0	90	0.68	1.69	0.059	0.50	1.26	3.33	1.30	0.74
7.17	159.9	120	0.69	1.04	0.023	0.44	0.84	1.92	1.33	0.64
7.43	319.9	120	0.41	0.65	0.019	0.36	0.57	1.15	1.12	0.88
7.35	588	150	0.34	0.40	0.0054	0.30	0.38	1.08	1.08	0.88

[a] $I_a = 5.5 \times 10^{10}[P]$ photons $cm^{-3}\ s^{-1}$ for [P] in torr.

Experiments with added helium were also performed. At the time of these experiments the cell was not properly conditioned and the mass balance relation was erratic. In Table 5 we report the C_2H_4, CO_2 and $C_2H_5CO_3H$ quantum yields which are used to support reactions of the $C_2H_5CO_3$ radical which are independent of wall conditions.

Results in the presence of NO were also done before the wall conditioning with I_2, and the results are given in Table 6. The main point of these experiments was to see whether the $C_2H_5CO_2$ radical had a sufficient lifetime to be scavenged by NO. The failure of the NO to suppress the CO_2 yield indicates that $C_2H_5CO_2$ was not scavenged. As mentioned before, $\Phi(C_2H_5CO_3H)$ was reduced to below our detection limit.

Finally a series of runs was done with *cis*-2-C_4H_8 present. These runs, listed in Table 7, were done after the I_2-conditioning experiments, so only the CO yields are reported. Again, butene reduces $\Phi(CO)$ to a value of 0.2 at the highest pressure used. It is difficult to say whether or not this is a lower limiting value for $\Phi(CO)$.

Approximate half-quenching pressures for the various gases are given in Table 8. The reported value for C_2H_5CHO could be considerably lower in view of the large uncertainty as a result of the vapor pressure constraints and the large degree of secondary decay in the experiments where the amount of C_2H_5CHO was varied.

TABLE 5

Effect of helium on the photo-oxidation of C_2H_5CHO[a]

[P] (Torr)	[O_2] (Torr)	[He] (Torr)	$\Phi(CO_2)$	$\Phi(C_2H_4)$	$\Phi(C_2H_5CO_3H)$
10.90	12.70	0	3.60	0.50	6.59
10.54	12.22	4.7	2.49	0.35	6.61
10.31	13.09	10.8	2.47	0.31	5.16
10.93	14.24	26.4	2.03	0.21	6.37
11.01	12.69	50.2	2.14	0.22	6.91
10.32	13.53	100.4	1.84	0.141	7.40
10.61	13.22	301.3	1.71	0.027	6.73
10.74	12.65	573.6	1.37	0.024	6.44

[a]Irradiation time, 50 min; I_a = 1.9×10^{11} photons cm^{-3} s^{-1}.

4. Discussion

4.1. Primary process

The CO quantum yield is a direct measure of the primary process. Since no C_2H_6 is formed, all the products are formed through free-radical precursors.

TABLE 6

Photo-oxidation of C_2H_5CHO in the presence of NO[a]

[P] (Torr)	[NO] (Torr)	Irradiation time (min)	I_a ($\times 10^{12}$ photons cm^{-3} s^{-1})	$\Phi(CO)$	$\Phi(CO_2)$	$\Phi(C_2H_4)$	$\Phi(CH_3CHO)$	$\Phi(C_2H_5OH)$ I
[NO] = 0.15 Torr								
2.27	0.152	240	0.15	0.83	0.81	0.078	0.153	0.92 1.53
5.52	0.152	60	0.37	0.56	0.92	0.119	0.168	1.40 0.94
11.3	0.153	40	0.76	0.60	0.82	0.022	0.109	1.66 0.80
22.0	0.149	30	1.48	0.61	0.85	0.010	0.093	1.22 1.11
44.2	0.153	20	2.97	0.44	0.76	0.0050	0.062	0.98 1.15
82.9	0.152	10	5.57	0.35	0.61	0.0023	0.036	1.13 0.82
124.8	0.150	10	8.41	0.16	0.52	0.0008	0.028	0.76 0.86
[P] = 11 Torr								
10.9	0.076	45	0.73	0.74	0.63	0.020	0.165	1.06 1.12
10.5[b]	0.120	30	0.70	0.77	—	—	0.22	1.48 —
11.3	0.153	40	0.76	0.60	0.82	0.022	0.109	1.66 0.80
10.8	0.300	60	0.72	0.76	1.00	0.023	0.123	1.41 1.15

[a] $[O_2] = 11.0 \pm 0.6$ Torr.
[b] $[O_2] = 14.2$ Torr.

TABLE 7

Photo-oxidation of C_2H_5CHO in the
presence of cis-2-C_4H_8[a]

[C_4H_8] (Torr)	[O_2] (Torr)	Irradiation time (h)	Φ(CO)
0	4.88	0.83	0.90
5.3	5.33	2.00	0.80
31.1	5.21	1.50	0.70
49.9	5.29	5.00	0.61
99.8	5.44	3.58	0.51
122	5.27	3.00	0.36
253	5.23	8.00	0.34
395	5.30	5.00	0.26
561	5.32	7.00	0.22
673	5.39	7.00	0.19
420	50.7	5.00	0.19
455	183	7.25	0.17
456	321	8.00	0.17

[a] [P] = 10.5 ± 0.5 Torr; I_a = 5.0 × 10^{12}
photons cm^{-3} s^{-1}.

TABLE 8

Half-quenching pressures

Compound	Half-quenching pressure (Torr)
C_2H_5CHO	160 ± 30
O_2	120 ± 20
Air	250 ± 30
Cis-2-C_4H_8	113 ± 10

Figure 1 shows a Stern–Volmer plot of the reciprocal CO quantum yield *versus* total pressure. The various gases have been weighted so that the initial slope is the same for all the gases. Thus the total pressure [M] is taken to be [air] + 2[O_2] + 1.5[P] + 2.2[cis-2-C_4H_8] where P represents propionaldehyde. The data in Fig. 1 show that Φ(CO)$^{-1}$ increases linearly with [M] at low [M] but that the rate of increase is diminished at higher [M]. In fact with O_2 as the major gas there may be a high pressure limiting value of about 3 - 4 for Φ(CO)$^{-1}$. A high pressure limiting value has been reported previously in the photolysis of butyraldehyde [14].

The data suggest a two-state mechanism for CO formation. It is known that both singlet and triplet states exist [10, 15]. However, we rule out the singlet state since Borkowski and Ausloos [15] have shown that propion-
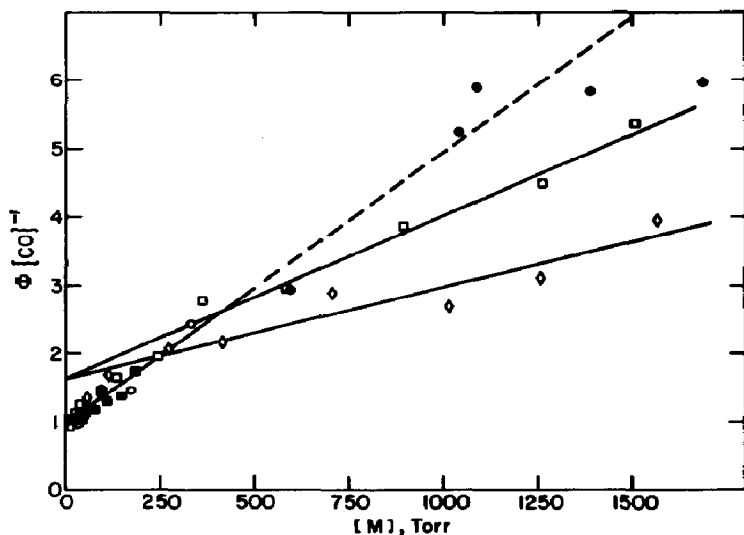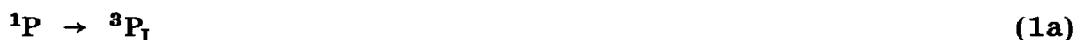
Fig. 1. Plot of the reciprocal CO quantum yield *vs.* total pressure [M] where [M] = [air] + 2[O$_2$] + 1.5[P] + 2.2[*cis*-2-C$_4$H$_8$] for various quenching gases: ○, air; □, *cis*-2-C$_4$H$_8$; ■, C$_2$H$_5$CHO; ◇, O$_2$; ●, O$_2$-*cis*-2-C$_4$H$_8$.

aldehyde singlet state fluorescence is not pressure quenched. The ground level triplet state can also be ruled out because its concentration is enhanced by an increase in pressure [15]. Furthermore, both O$_2$ and *cis*-2-C$_4$H$_8$ should quench the triplet much more efficiently than shown for either of the two reacting states. However, the quenching of the triplet state by O$_2$ might lead directly to product formation:

$$^3P + O_2 \rightarrow C_2H_5 + CO + HO_2 \tag{3}$$

where ^{3}P represents triplet propionaldehyde. In this case there would be a competition between *cis*-2-C$_4$H$_8$ and O$_2$, and increasing the [O$_2$]-to-[*cis*-2-C$_4$H$_8$] ratio should increase Φ(CO), contrary to the observations.

We conclude that all the dissociation comes from the manifold of levels in the vibrationally excited triplet state and that these levels are quenched with different efficiencies. These states are formed directly by internal conversion from the initially formed singlet state. A simple two-level representation is given by

$$P + h\nu \rightarrow {}^1P \qquad\qquad \text{rate, } I_a$$

$$^1P \rightarrow {}^3P_I \tag{1a}$$

$$^1P \rightarrow {}^3P_{II} \tag{1b}$$

$$^3P_I \rightarrow C_2H_5 + HCO \tag{4a}$$

$$^3P_I + M \rightarrow \text{deactivation} \tag{4b}$$

$$^3P_{II} \rightarrow C_2H_5 + HCO \tag{5a}$$

$$^3P_{II} + M \rightarrow \text{deactivation} \tag{5b}$$

where ^1P, ^3P_I and $^3P_{II}$ represent respectively the excited singlet state and the slowly and rapidly quenched levels of the vibrationally excited triplet state. This mechanism leads to the rate law

$$\Phi(CO) = \frac{\phi_{1a}k_{4a}}{k_{4a} + k_{4b}[M]} + \frac{\phi_{1b}k_{5a}}{k_{5a} + k_{5b}[M]}$$

At high pressures the last term is negligible and

$$\Phi(CO)^{-1} \approx \phi_{1a}^{-1}\left(1 + \frac{k_{4b}[M]}{k_{4a}}\right)$$

From Fig. 1, the data indicate that $\phi_{1a} = 0.60$ and that k_{4b}/k_{4a} is about 1.6×10^{-3} Torr^{-1} for $[M] = [O_2]$ and about 3.7×10^{-3} Torr^{-1} for $[M] \approx [cis\text{-}2\text{-}C_4H_8]$. At low pressures $k_{4b}[M]/k_{4a}$ is negligible and
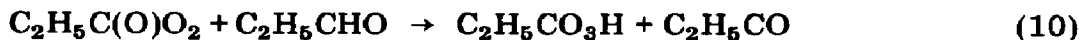
$$\{\Phi(CO) - \phi_{1a}\}^{-1} \approx \phi_{1b}^{-1}\left(1 + \frac{k_{5b}[M]}{k_{5a}}\right)$$

From the data, $k_{5a}/k_{5b} \approx 70$ Torr for $[M] = [air] + 2[O_2] + 1.5[P] + 2.2[cis\text{-}2\text{-}C_4H_8]$. This value is similar to that of 105 Torr found for the quenching enhancement of triplet emission from the data of Borkowski and Ausloos [15].

One point of interest in Fig. 1 is that the quenching in mixtures containing a large amount of both O_2 and $cis\text{-}2\text{-}C_4H_8$ is greater than expected from the sum of their individual contributions. This suggests that some levels slowly quenched by one gas may be rapidly quenched by the other gas and vice versa.

4.2. Secondary process

The expected secondary reactions are

$$HCO + O_2 \rightarrow HO_2 + CO \tag{2}$$

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2 \tag{6}$$

$$C_2H_5O_2 + RO_2 \rightarrow C_2H_5O + RO + O_2 \tag{7}$$

$$C_2H_5O + C_2H_5CHO \rightarrow C_2H_5OH + C_2H_5CO \tag{8}$$

$$C_2H_5CO + O_2 \rightarrow C_2H_5C(O)O_2 \tag{9}$$

$$C_2H_5C(O)O_2 + C_2H_5CHO \rightarrow C_2H_5CO_3H + C_2H_5CO \tag{10}$$

$$C_2H_5C(O)O_2 + HO_2 \rightarrow C_2H_5CO_3H + O_2 \tag{11}$$

$$C_2H_5C(O)O_2 + RO_2 \rightarrow C_2H_5C(O)O + RO + O_2 \tag{12}$$

$$C_2H_5C(O)O \rightarrow C_2H_5 + CO_2 \tag{13}$$

$$RO_2 \rightarrow \text{termination} \tag{14}$$

$$C_2H_5O \rightarrow \text{termination} \tag{15}$$
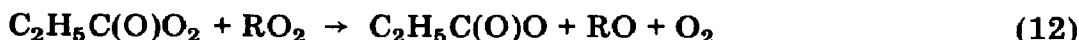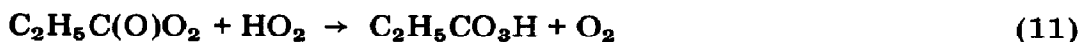
$$HO_2 \rightarrow \text{termination} \tag{16}$$

where RO_2 represents either organic peroxy radical. The three radical termination steps may occur by radical–radical reactions in the gas phase or on the wall. The CH_3CHO produced is formed in these termination steps (primarily reaction (15)) or from the secondary decay of $C_2H_5C(O)O_2H$ when $\Phi(C_2H_5C(\dot{O})O_2H)$ is very large.
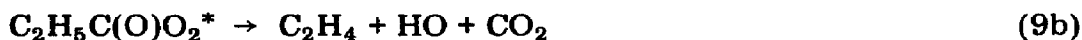
The above mechanism gives one CO molecule for each primary decomposition, and thus $\Phi(CO)$ gives the primary quantum yield. There is a chain process involving C_2H_5O and $C_2H_5C(O)O_2$ radicals which gives CO_2, C_2H_5OH and $C_2H_5CO_3H$. The data in the tables show that their quantum yields often exceed those of CO, confirming that they are products of a chain reaction.

The CH_3CHO is not produced in a chain step and therefore $\Phi(CH_3CHO)/\Phi(CO)$ should be equal to unity or less. This quantity is given in the tables. Usually it is less than or close to 1.0.

Su and coworkers [5, 16] have found that HO_2 adds to CH_2O to produce HCOOH. We see no evidence for the analogous reaction between HO_2 and C_2H_5CHO, since $C_2H_5CO_2H$ is not produced at high values of the ratio $[O_2]/[C_2H_5CHO]$ where the chain length approaches zero, yet HO_2 radicals must be present. From the dependence of the $C_2H_5CO_3H$ quantum yields on C_2H_5CHO pressure in the first set of experiments in Table 1 where the C_2H_5OH quantum yields remain constant, it is clear that reaction (10) is important.

The mechanism outlined above does not account for C_2H_4 formation. The obvious reaction for C_2H_4 formation is abstraction of a hydrogen atom from C_2H_5 by O_2. In a separate study [17] we have examined the photo-oxidation of C_2H_5I and have found such a reaction to be completely negligible at room temperature at pressures above 2 Torr. Thus the C_2H_4 must come from elsewhere.

Baldwin and coworkers [18, 19] have postulated that in combustion reactions C_2H_4 is produced from the reaction of C_2H_5CO with O_2:

$$C_2H_5CO + O_2 \rightarrow C_2H_5C(O)O_2^* \tag{9a}$$

$$C_2H_5C(O)O_2^* \rightarrow C_2H_4 + HO + CO_2 \tag{9b}$$

$$C_2H_5C(O)O_2^* + M \rightarrow C_2H_5C(O)O_2 \tag{9c}$$

Reaction (9b) could proceed through the six-membered ring intermediate
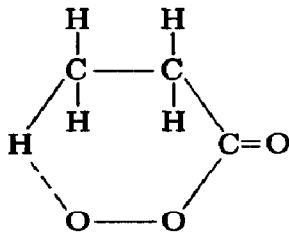
which cleaves to give C_2H_4, CO_2 and HO. The HO radicals regenerate the chain via

$$HO + C_2H_5CHO \rightarrow H_2O + C_2H_5CO \tag{17}$$

The mechanism including reactions (9a) - (9c) leads to the rate law

$$\frac{\Phi(C_2H_5CO_3H) + \Phi(CO_2) - \Phi(C_2H_4)}{\Phi(C_2H_4)} = \frac{k_{9c}[M]}{k_{9b}}$$

Figure 2 is a log–log plot of the left-hand side of this equation *versus* [M] where [M] has been taken to be [P] + [O$_2$] + 0.3[He] + 0.5[air]. The data are badly scattered, but a trend is obvious. The data points are fitted to a line of slope 1.0. The intercept gives k_{9c}/k_{9b} = 1.2 Torr^{-1}.
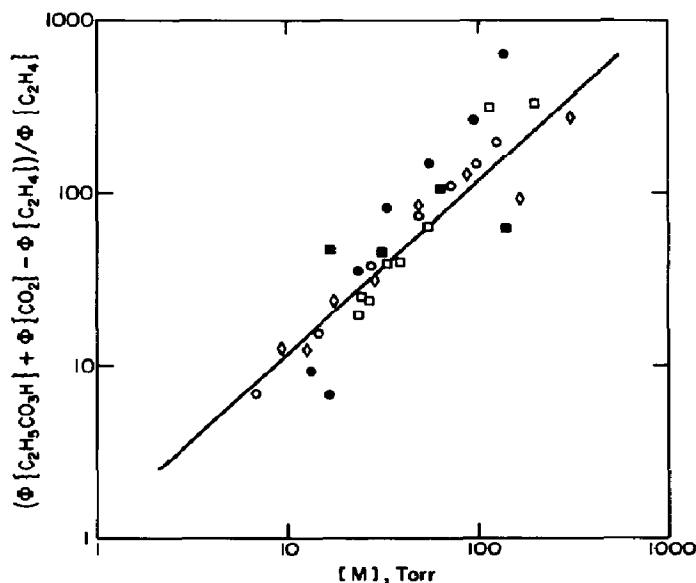

Fig. 2. Log–log plot of $\{\Phi(C_2H_5CO_3H) + \Phi(CO_2) - \Phi(C_2H_4)\}/\Phi(C_2H_4)$ vs. total pressure [M] where [M] = [P] + [O$_2$] + 0.3[He] + 0.5[air] for various quenching gases: □, helium; ◊, air; ■, O$_2$; ○, C$_2$H$_5$CHO; ●, C$_2$H$_5$CHO with NO present.

Acknowledgments

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