

THE FREE RADICAL OXIDATION OF CH₂O IN THE PRESENCE OF NO₂ AND NO

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Summary

NO₂ was photolyzed at 366 nm and 296 K in the presence of CH₂O and O₂ and in some runs with added NO or N₂. The measured products were CO, CO₂ and HCOOH. H₂ and N₂O were not produced. Both the CO and the CO₂ were produced in a linear fashion with irradiation time, but the HCOOH grew after a marked induction period. From the CO₂ quantum yields at high [O₂]/[NO₂] ratios an upper limiting value of 0.16 ± 0.02 was found for k_{3b}/k_3 where reactions (3a) and (3b) are



This is lower than the value of approximately 0.30 reported for k_{3b}/k_3 by Chang and Barker. From the CO and CO₂ yields the competition for HCO between O₂ and NO₂ could be measured.



The ratio k_9/k_{7a} was found to be 0.21 ± 0.07 and was independent of pressure. The analysis required knowledge of some other rate coefficients. If those rate coefficients are completely in error, k_9/k_{7a} could be as high as 0.63. With the literature value of $5.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for k_9 , the best value for k_{7a} is $(2.7 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ with a lower limiting value of $(8.9 \pm 3.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

Information was also obtained on the reaction of HO₂ with CH₂O which produces HCOOH. An approximate value of $(1.4 - 3.2) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ was found for the rate coefficient for this reaction which is about 14 - 32 times greater than the estimate of Su *et al.*

1. Introduction

HCOOH has been measured in polluted atmospheres [1]. Many researchers have studied the photooxidation of CH₂O under various conditions and have observed HCOOH as a product [2 - 8]. However, the mechanism of HCOOH formation has remained quite elusive. Previous work in our laboratory [5] has indicated the possibility of HCO reacting with O₂ eventually to produce HCOOH. However, most researchers now agree that this reaction produces CO and HO₂ exclusively. Recent work in our laboratory [9] has shown that the reaction of HO with CH₂O does not lead to HCOOH production. Su and coworkers [7, 8] have recently published results that indicate that the HO₂ radical is responsible for HCOOH formation.

There have been two published studies on the photooxidation of CH₂O in the presence of nitrogen oxides. Bufalini and Brubaker [10] photolyzed mixtures of CH₂O and NO₂ in air. With a ratio of CH₂O to NO₂ of 10:1, they detected H₂O₂ and CO but only a little HCOOH. They photolyzed some mixtures in the absence of NO₂ and reported that the yields of H₂O₂ increased. It is obvious now, but was not at the time of their work, that HO₂ radicals would be scavenged by NO₂ and this would reduce the yield of H₂O₂. Hanst and Gay [11] photolyzed Cl₂-NO₂-CH₂O mixtures in air. With a [CH₂O]/[NO₂] ratio of less than unity they observed a variety of products, including HO₂NO₂, but no HCOOH was observed.

This study was undertaken in order to determine the effect of NO₂ on HCOOH formation. Various ratios of CH₂O to NO₂ were photolyzed in the presence of O₂ and the results are quite consistent with previous work. Also, by varying the [O₂]/[NO₂] ratio the rate constant for the reaction of HCO with NO₂ was determined relative to the rate constant of the reaction of HCO with O₂.

Chang and Barker [12] have reported that O(³P) reacts with CH₂O to give CO₂ with 30% efficiency. We also found that CO₂ was produced, even at our highest [O₂]/[NO₂] ratios, permitting us to put an upper limit to the efficiency of this reaction.

2. Experimental

NO₂ was photolyzed at 296 K in the presence of CH₂O, O₂ and NO using 366 nm radiation from a mercury lamp. At this wavelength no products (CO, CO₂, H₂ or HCOOH) were found in the absence of NO₂. Actinometry was performed by monitoring the decay of NO₂ in the absence of CH₂O and O₂; the quantum yield of NO₂ disappearance is 2.0 under these conditions.

The experimental apparatus and purification procedures for the gases used in the study have been described previously [6, 9]. Photolysis took place within a long-path IR cell. The changes in pressure of NO₂ and

HCOOH were monitored by *in situ* IR analysis. An external chart recorder was used to follow the change in absorbance as a function of time of either NO₂ or HCOOH. Only one of these species could be monitored continuously throughout a given run. In most experiments the HCOOH was monitored continuously and the change in NO₂ pressure was determined after the photolysis was terminated. CO, CO₂, H₂ and N₂O were monitored by gas chromatography during and after photolysis.

The dark polymerization of CH₂O, which was insignificant in the absence of O₂, occurred to a greater extent when O₂ was present, but this caused no difficulty.

3. Results

NO₂ was photolyzed at 296 K in the presence of CH₂O and O₂ using 366 nm radiation. Many experiments were performed with NO also added initially. Since NO is a product of NO₂ photolysis, NO was present during all the experiments whether it was added initially or not. In all the experiments the CH₂O pressure was between 1.35 and 2.86 Torr.

The products measured were CO, CO₂ and HCOOH. The change in NO₂ pressure was also measured. We looked for, but did not find, H₂ and N₂O. Because it was difficult to analyze for NO, this species was not monitored.

In one series of runs, shown in Table 1, the O₂ pressure was held constant at approximately 52 Torr. The initial NO and NO₂ pressures were varied from 0 to 29.9 mTorr and from 10.4 to 238 mTorr respectively. In these experiments, done for irradiation times of 1 - 4.5 h, no CO₂ was found and an upper limit of 0.15 ± 0.03 can be placed on the adjusted CO₂ quantum yield $\Phi(\text{CO}_2)/\xi$, where ξ is the fraction of O(³P) produced which reacts with CH₂O. In experiments done under comparable conditions, but for longer irradiation times (given in Table 2), $\Phi(\text{CO}_2)/\xi$ was found to be 0.16 ± 0.02 . Thus this value is an upper limit to the initial value, since some CO₂ could come from secondary oxidation of the other products.

For the runs in Table 1 CO was produced in a linear fashion with irradiation time and its quantum yields $\Phi(\text{CO})$ and $\Phi(\text{CO})/\xi$ are listed in Table 1. They tend to increase with the $[\text{NO}]/[\text{NO}_2]$ ratio. In contrast, HCOOH is not produced in a linear fashion with irradiation time. Figure 1 is a typical growth plot for HCOOH from which it is obvious that the HCOOH production has an induction period. We found that the HCOOH data in any run could be fitted to an expression of the form

$$[\text{HCOOH}] = \Phi(\text{HCOOH})_{\text{eff}} I_a [t - \tau \{1 - \exp(-t/\tau)\}] \quad (\text{I})$$

where I_a is the absorbed intensity, t is the irradiation time, $\tau \approx 0.75$ h and $\Phi(\text{HCOOH})_{\text{eff}}$ is the limiting quantum yield of HCOOH formation obtained from the slope of a plot of $[\text{HCOOH}]$ against the term in parentheses in eqn. (I). Such a plot is shown in Fig. 2. Values of $\Phi(\text{HCOOH})_{\text{eff}}$ and

TABLE 1

Product quantum yields from the photolysis of NO_2 at 366 nm in the presence of NO , CH_2O and O_2

$[\text{NO}]$ (mTorr)	$[\text{NO}_2]$ (mTorr)	$[\text{CH}_2\text{O}]$ (Torr)	$[\text{O}_2]$ (Torr)	$\frac{[\text{NO}]}{[\text{NO}_2]}$	$\frac{[\text{CH}_2\text{O}]}{[\text{NO}_2]}$	Irradiation time (h)	I_a (mTorr h^{-1})	$\Phi(\text{CO})$	$\Phi(\text{HCOOH})_{\text{est}}$	$\Phi(\text{NO}_2)$	ξ	δ	$\frac{\Phi(\text{CO})}{\xi}$	$\frac{\Phi(\text{HCOOH})_{\text{est}}}{\xi}$
0	50.9	1.76	52.1	0	34.6	1.0	0.838	0.251	15.4	0	0.335	0.554	0.75	46.0
0	52.9	1.76	46.9	0	33.3	5.5	0.876	1.20	6.49	-2.15	0.332	0.612	3.61	19.5
0	52.9	1.80	51.5	0	34.0	1.0	0.876	1.12	9.28	-9.4	0.333	0.569	3.36	27.9
0	52.9	2.39	52.7	0	45.2	3.0	0.876	0.533	15.4	-2.28	0.397	0.554	1.34	38.9
0	53.9	1.60	51.8	0	29.7	4.5	0.895	0.860	7.45	-1.76	0.303	0.572	2.84	24.6
0	54.9	1.60	51.7	0	29.1	3.0	0.914	0.766	8.35	-1.94	0.300	0.577	2.55	27.8
0	55.9	2.23	54.1	0	39.9	3.0	0.933	0.827	20.3	-1.10	0.368	0.556	2.25	55.2
0	78.8	1.97	52.4	0	25.0	3.0	1.11	0.965	-	-5.92	0.275	0.654	3.51	-
1.16	57.9	2.11	48.1	0.0200	36.4	3.0	0.971	1.05	8.58	-0.73	0.353	0.620	2.98	24.3
3.83	54.3	2.23	50.7	0.0705	41.1	3.0	0.903	2.10	22.4	-2.08	0.377	0.579	5.57	59.4
4.39	16.0	2.18	54.5	0.274	136	3.0	0.175	-	66.7	-1.23	0.609	0.261	-	110
4.99	174	1.63	53.7	0.0287	9.37	3.0	2.60	0.885	0.423	-1.70	0.129	0.800	6.80	3.28
5.94	54.9	2.50	48.4	0.108	45.5	3.0	0.914	2.14	26.2	-3.07	0.404	0.601	5.30	64.9
6.38	15.0	2.44	51.6	0.425	163	3.0	0.130	11.0	98.2	+2.09	0.652	0.268	16.9	151
6.98	10.4	2.40	53.4	0.671	231	3.0	0.072	16.7	174	-6.75	0.697	0.192	30.0	249
6.98	21.9	1.94	51.6	0.319	88.6	3.0	0.212	7.26	45.4	0	0.535	0.351	13.6	84.9
7.18	29.9	2.21	52.1	0.240	73.9	3.0	0.439	5.01	22.1	-1.24	0.499	0.419	10.0	44.3
8.13	56.9	2.22	55.8	0.143	39.0	3.0	0.952	2.29	20.4	-0.735	0.362	0.546	6.33	56.4
8.23	19.6	2.54	58.4	0.42	130	3.0	0.175	10.9	-	-	0.609	0.252	17.9	-
8.38	94.8	1.90	52.2	0.0884	20.0	1.0	1.67	1.14	5.16	-6.68	0.235	0.696	4.85	22.0
8.98	47.9	2.62	47.2	0.187	54.7	2.0	0.781	3.02	-	-	0.446	0.579	6.77	-
8.98	107	1.35	52.8	0.0839	12.6	3.0	1.55	1.94	0.86	-3.85	0.163	0.720	11.9	5.28
9.97	51.9	1.99	53.6	0.192	38.3	1.0	0.857	2.05	9.33	-2.42	0.357	0.544	5.74	26.1
9.97	114	1.87	52.0	0.0875	16.4	1.0	2.04	1.22	-	-10.2	0.203	0.736	6.01	-
9.97	238	2.19	51.2	0.0419	9.20	3.0	3.60	0.833	0.60	-5.68	0.128	0.855	6.51	4.69
10.4	73.2	2.04	53.3	0.142	27.9	1.0	1.26	1.39	8.12	-5.70	0.295	0.629	4.71	27.5
10.4	76.8	1.96	51.9	0.135	25.5	1.0	1.33	1.45	-	-3.58	0.279	0.652	5.20	-
11.0	20.9	1.94	54.1	0.526	92.8	1.25	0.268	9.40	53.3	-12.3	0.534	0.321	17.6	99.8

TABLE 1 (continued)

[NO] (mTorr)	[NO ₂] (mTorr)	[CH ₂ O] (Torr)	[O ₂] (Torr)	[NO] [NO ₂]	[CH ₂ O] [NO ₂]	Irradi- ation time (h)	I _a (mTorr h ⁻¹)	Φ(CO) Φ(HCOOH) _{eff}	Φ(NO ₂) ξ	δ	Φ(CO) ξ	Φ(HCOOH) _{eff} ξ	
11.0	29.9	1.93	54.3	0.368	64.5	1.0	0.439	6.29	24.1	0.462	0.401	13.6	52.2
12.0	34.1	1.84	49.9	0.352	54.0	1.0	0.519	5.36	22.0	0.430	0.474	12.5	51.2
13.0	198	1.85	51.6	0.0657	9.34	1.0	3.63	0.595	1.61	—	0.129	0.830	4.61
14.0	19.5	2.26	51.9	0.718	116	3.0	0.174	12.6	52.7	1.80	0.589	0.321	21.4
16.8	132	2.28	52.1	0.127	17.3	3.0	1.94	1.49	4.03	—	0.212	0.760	7.03
17.0	24.9	1.88	53.3	0.683	75.5	1.25	0.344	10.3	37.4	—	0.494	0.367	20.9
18.0	145	2.06	52.0	0.124	14.2	3.0	2.14	1.36	2.14	—	0.182	0.779	7.47
19.0	162	2.04	53.2	0.117	12.6	3.0	2.41	1.35	0.57	—	0.165	0.790	8.18
29.3	47.9	2.32	47.8	0.612	48.4	3.1	0.781	6.84	—	—	0.416	0.575	16.4
29.9	46.9	2.36	57.8	0.638	50.3	3.0	0.762	5.31	20.2	—	0.414	0.480	12.8

TABLE 2

The effect of decreasing O_2 pressure on the product quantum yields from the photolysis of NO_2 at 366 nm in the presence of CH_2O , O_2 and N_2

$[O_2]$ [NO_2]	[NO_2] (mTorr)	[CH_2O] (Torr)	[O_2] (Torr)	[N_2] (Torr)	Irradiation time (h)	I_a (mTorr h^{-1})	$\Phi(CO)$	$\Phi(CO_2)$	$\Phi(NO_2)$	ξ	$\frac{\Phi(CO)}{\xi}$	$\frac{\Phi(CO_2)}{\xi}$
<i>Total pressure = 54 Torr</i>												
2438	21.9	2.06	53.4	0	8.0	0.212	2.38	0.088	-1.53	0.541	4.40	0.16
917	59.2	1.91	54.3	0	6.5	0.797	1.58	0.055	-2.00	0.321	4.92	0.17
617	57.5	2.30	35.5	17.7	6.0	0.771	1.65	0.068	—	0.378	4.37	0.18
171	59.8	2.14	10.2	42.7	6.0	0.807	1.70	0.084	-2.95	0.365	4.66	0.23
96.5	53.9	2.31	5.20	47.6	6.0	0.714	1.86	0.106	-2.03	0.409	4.55	0.26
50.9	51.9	2.03	2.64	50.9	6.0	0.683	1.85	0.152	-1.19	0.389	4.76	0.39
23.4	53.9	1.91	1.26	51.1	6.0	0.714	1.81	0.235	—	0.367	4.93	0.64
11.2	53.9	2.22	0.604	51.7	6.25	0.714	1.88	0.422	-3.61	0.402	4.67	1.05
4.96	56.5	2.18	0.280	52.0	6.0	0.755	1.57	0.561	-3.26	0.387	4.06	1.45
0.780	56.9	1.95	0.0444	51.7	6.0	0.761	1.29	0.718	-3.22	0.359	3.59	2.00
<i>Total pressure = 2.7 Torr</i>												
9.65	59.8	1.80	0.577	0	6.0	0.807	3.08	0.794	-2.73	0.330	9.33	2.41
4.87	49.9	2.86	0.243	0	6.0	0.651	3.23	1.09	-2.83	0.484	6.67	2.25
3.93	54.9	2.34	0.216	0	6.0	0.730	2.49	0.980	-3.00	0.411	6.06	2.38
3.27	61.8	2.59	0.202	0	6.0	0.838	2.45	0.974	-2.66	0.407	6.02	2.39
1.58	55.3	2.61	0.0874	0	6.0	0.736	2.31	1.13	-3.09	0.436	5.30	2.59
0.992	52.9	2.10	0.0525	0	6.0	0.699	1.94	1.10	-4.37	0.394	4.92	2.79

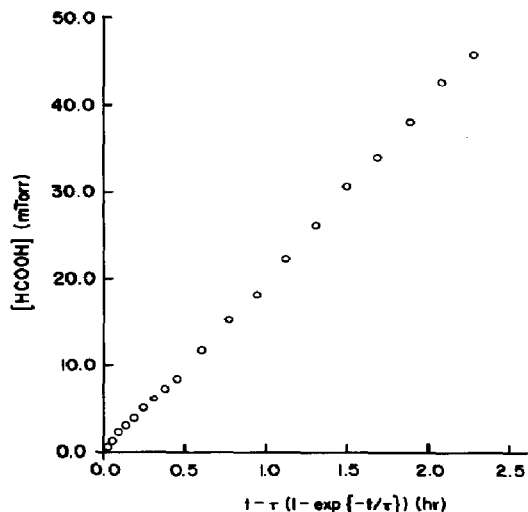
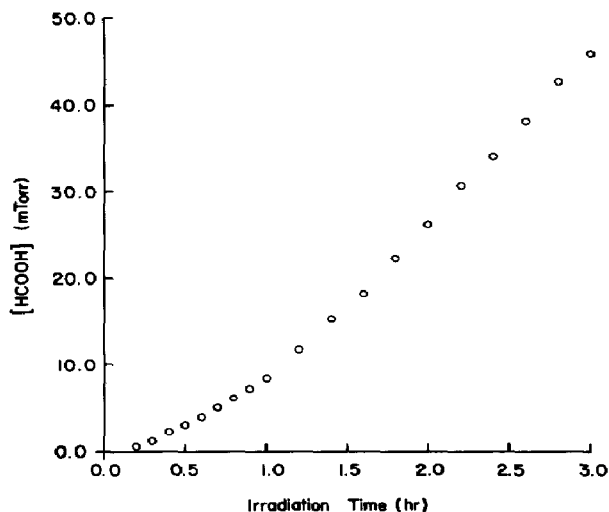


Fig. 1. Plot of $[\text{HCOOH}]$ vs. irradiation time for initial reactant concentrations of 3.83 mTorr NO, 54.3 mTorr NO_2 , 2.23 Torr CH_2O and 50.7 Torr O_2 .

Fig. 2. Plot of $[\text{HCOOH}]$ vs. $t - \tau\{1 - \exp(-t/\tau)\}$ for the data from Fig. 1 with $\tau = 0.75$ h.

$\Phi(\text{HCOOH})_{\text{eff}}/\xi$ obtained from such plots for each run are given in Table 1. The quantity $\Phi(\text{HCOOH})_{\text{eff}}/\xi$ increases with the $[\text{CH}_2\text{O}]/[\text{NO}_2]$ ratio. At the lowest $[\text{CH}_2\text{O}]/[\text{NO}_2]$ ratios a lot of scatter is present in the data. However, it is clear that only a small amount of HCOOH is produced. This is in good agreement with the results of Bufalini and Brubaker [10] and Hanst and Gay [11].

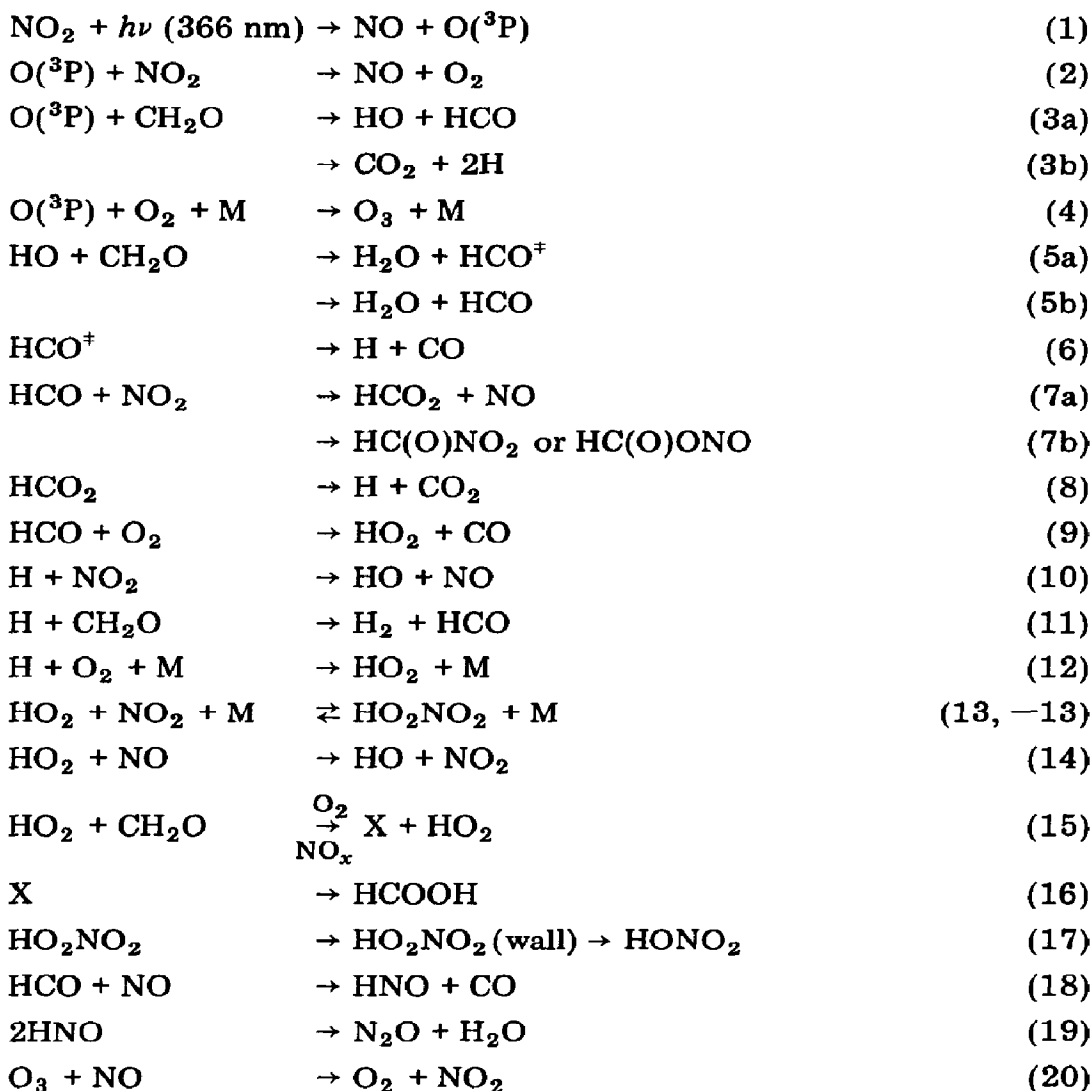
The NO_2 pressure was seen to decrease in every experiment except those with high initial $[\text{NO}]$. The decrease was about 10% on the average. At high initial $[\text{NO}]$ sufficient NO is oxidized to NO_2 so that either no change or an increase in NO_2 pressure was observed.

A second series of runs was done with no NO added in which the NO_2 and CH_2O pressures were held fairly constant and the O_2 pressure was varied. These are reported in Table 2. One set of runs was done at a constant total pressure of approximately 54 Torr, N_2 being added to maintain the pressure. In the other set the total pressure was kept at approximately 2.7 Torr.

The products measured for the runs in Table 2 were CO and CO_2 and both increased proportionately to the irradiation time. The values of $\Phi(\text{CO})/\xi$ do not change much with the $[\text{O}_2]/[\text{NO}_2]$ ratio, but $\Phi(\text{CO}_2)/\xi$ rises markedly from a lower limiting value of 0.16 at high $[\text{O}_2]/[\text{NO}_2]$ ratios to values in excess of 2.0 at low $[\text{O}_2]/[\text{NO}_2]$ ratios.

4. Discussion

The reaction mechanism postulated below is the mechanism from an earlier publication [9] with reactions added because of the presence of O_2 .



Here HCO^\ddagger is a vibrationally excited radical that rapidly decomposes even in an atmosphere of added gas [9, 13]. All these reactions, with the exception of reactions (15) and (16), are well known.

Reactions (15) and (16), which include some unspecified intermediate X, are not fundamental reactions but reflect the fact that HCOOH must be produced in a chain reaction which regenerates HO_2 to account for its high yields. The intermediate X is needed to account for the induction period in HCOOH formation. This is in agreement with recent work published by Su and coworkers [7, 8]. They have shown through the use of Fourier transform IR spectroscopy that the reaction of HO_2 with CH_2O must lead to a metastable intermediate which would decay to HCOOH .

Some simplification can be made in the mechanism. Under our conditions reaction (18) could never compete with reaction (9) since the rate coefficients are comparable [14]. Furthermore no N_2O was found so that reactions (18) and (19) can be discarded. Since no H_2 was found, reaction (11) cannot be important. This is consistent with the known rate coefficients for reactions (10) - (12) [15].

CO_2 is produced in reactions (3b) and (8). At high $[O_2]/[NO_2]$ ratios all the HCO is scavenged by O_2 , so that HCO_2 production and consequently reaction (8) are negligible. Under these conditions the mechanism predicts

$$\Phi(CO_2)/\xi = k_{3b}/k_3 \quad (II)$$

where ξ is the fraction of $O(^3P)$ that reacts with CH_2O , *i.e.*

$$\xi \equiv k_3[CH_2O]/(k_2[NO_2] + k_3[CH_2O] + k_4[O_2][M])$$

Values of ξ can be computed since at room temperature $k_2 = 9.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $k_3 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ and $k_4 = 6.3 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$ [15]. For the runs in Table 1 no CO_2 was found, which leads to an upper limiting value for $\Phi(CO_2)/\xi$ and k_{3b}/k_3 of 0.15 ± 0.03 from the sensitivity of our analytical technique. For longer exposure runs (see Table 2) CO_2 was found with $\Phi(CO_2)/\xi = 0.16 \pm 0.02$ at the highest $[O_2]/[NO_2]$ ratios. This value should be considered to be an upper limit to k_{3b}/k_3 since some CO_2 might come from reaction (7a) followed by reaction (8), from secondary oxidation of CO or HCOOH or from some other reaction which is not considered in the mechanism. Our upper limit of 0.16 for k_{3b}/k_3 is considerably smaller than the value of approximately 0.30 reported by Chang and Barker [12].

Other workers [16 - 18] have observed CO_2 formation while studying reaction (3). Most of them have attributed the CO_2 formed to the reaction of $O(^3P)$ with HCO. This reaction is very fast [19] and yields CO_2 as a product with 42% efficiency [20]. However, under our experimental conditions of low light intensity, radical-radical reactions are not important and this source of CO_2 cannot be important in our work.

The mechanism leads to a straightforward rate law for the competition between O_2 and NO_2 for HCO since these reactions are the principal sources of CO and CO_2 respectively. The rate expression is

$$\left(\frac{\Phi(CO)}{\xi} - \frac{k_{5a}}{k_{5b}} \left[\frac{k_7}{k_{7a}} \left\{ \frac{\Phi(CO_2)}{\xi} - \frac{k_{3b}}{k_3} \right\} - \frac{k_{3a}}{k_3} \right] \right) \left[\left(1 + \frac{k_{5a}}{k_{5b}} \right) \left\{ \frac{\Phi(CO_2)}{\xi} - \frac{k_{3b}}{k_3} \right\} \right]^{-1} = \frac{k_9[O_2]}{k_{7a}[NO_2]} \quad (III)$$

This expression is valid as long as there are no sources of CO other than those given in the mechanism. The value of 0.16 is used for k_{3b}/k_3 , and this corrects for all other sources of CO_2 , whether it is the correct value or not, since it is just the correction term for the residual CO_2 found at high $[O_2]/[NO_2]$ ratios. Expression (III) is independent of the details of reactions (15) and (16) or of the nature of the terminating reactions.

In order to compute the left-hand side of eqn. (III) it is necessary to know k_{5a}/k_{5b} and k_7/k_{7a} . Our previous work [9] gave $k_{5a}/k_5 = 0.49$ and $k_{7a}/k_{7b} = 1.14$ for $k_{3b}/k_3 = 0$ or $k_{7a}/k_{7b} = 0.99$ for $k_{3b}/k_3 = 0.30$. With the value of 0.16 used here for k_{3b}/k_3 , k_{7a}/k_7 becomes 0.51 ± 0.06 . The left-hand side of eqn. (III) can be computed for the runs in Table 2 and can be plotted against the $[O_2]/[NO_2]$ ratios. This is done in Fig. 3. The logarithmic plot is fitted by one straight line of slope 1.0 for the data at both total pressures, thus indicating no significant pressure effects on the rate coefficients for reactions (5), (6), (7) or (9). The intercept gives $k_9/k_{7a} = 0.21 \pm 0.07$. (The intercepts for Figs. 3 - 5 refer to the values of the ordinate when the logarithm of the ratio of concentrations is zero, *i.e.* when the ratio is unity.) This result is not totally unexpected since NO_2 reacts faster with a number of free radicals than does O_2 [15]. No other absolute or relative rate coefficient measurements have been made on reaction (7). The reported value for k_9 is $5.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at room temperature [14, 19]. Thus $k_{7a} = (2.7 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

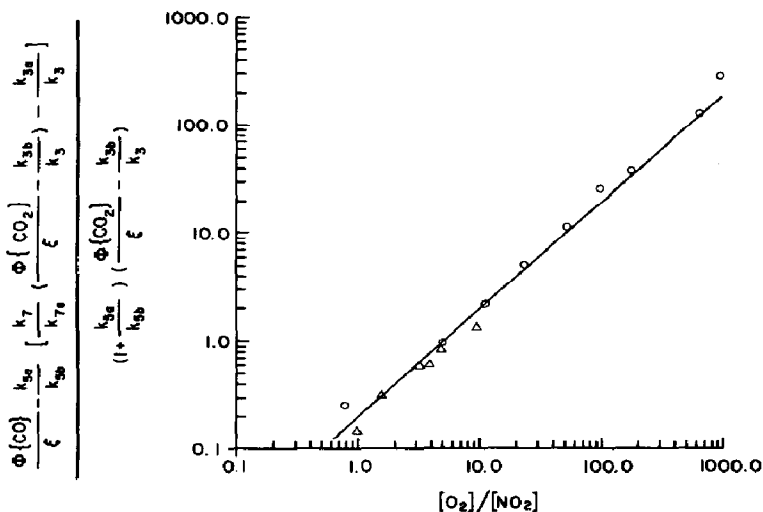


Fig. 3. Logarithmic plot of the left-hand side of eqn. (III) vs. the $[O_2]/[NO_2]$ ratio for the data in Table 2: \circ , total pressure 55.0 ± 0.8 Torr; \triangle , total pressure 2.67 ± 0.33 Torr. The rate coefficients used to compute the left-hand side of eqn. (III) were $k_{5a}/k_{5b} = 0.96$, $k_7/k_{7a} = 1.96$, $k_{3a}/k_3 = 0.84$ and $k_{3b}/k_3 = 0.16$.

This value of k_9/k_{7a} depends on the correctness of the values for k_{5a}/k_{5b} and k_7/k_{7a} . Thus we repeated the calculations of the left-hand side of eqn. (III) using limiting values for these rate coefficients (0 for k_{5a}/k_{5b} and 1.0 for k_7/k_{7a}) and we replotted the data (not shown). If k_7/k_{7a} is set at 1.0, but k_{5a}/k_5 kept at 0.49, k_9/k_{7a} becomes 0.28. If k_{5a}/k_5 is set at 0, a good straight line plot is obtained but k_9/k_{7a} rises to 0.63 and $k_{7a} \approx (8.9 \pm 3.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

Let us now consider CO and HCOOH formation in the presence of a large excess of O_2 . Under these conditions (Table 1) HCO does not react with

NO_2 and reactions (7) and (8) can be ignored. However, the details of reactions (15) and (16) are not known and the analysis that follows must be speculative. Nevertheless we should be able to obtain an estimate for k_{15} .

Application of the steady state assumption to free radicals (but not HO_2NO_2 or X) to the mechanism (omitting reactions (7), (8), (18) and (19)) leads to the expressions

$$\frac{d[\text{CO}]}{dt} = \left(\frac{k_{3a}}{k_3} + \frac{k_{3a}/k_3 + 2\delta k_{3b}/k_3}{1 - \delta k_{5a}/k_5} \right) \xi I_a + \frac{2\xi I_a k_{14} [\text{NO}]}{(1 - \delta k_{5a}/k_5) k_{13} [\text{NO}_2] [\text{M}]} \left[1 + \frac{k_{-13} [\text{M}]}{k_{17}} \left\{ 1 - \exp(-k_{17}t) \right\} \right] \quad (\text{IV})$$

$$\frac{d[\text{HCOOH}]}{dt} = \frac{2\xi I_a k_{15} [\text{CH}_2\text{O}]}{k_{13} [\text{NO}_2] [\text{M}]} \left[1 + \frac{k_{-13} [\text{M}]}{k_{17}} \left\{ 1 - \exp(-k_{17}t) \right\} \right] \times \{ 1 - \exp(-k_{16}t) \} \quad (\text{V})$$

where ξ is the fraction of $\text{O}(^3\text{P})$ that reacts with CH_2O as given earlier and δ is the fraction of hydrogen atoms that reacts with NO_2 , *i.e.*

$$\delta \equiv k_{10} [\text{NO}_2] / (k_{10} [\text{NO}_2] + k_{11} [\text{CH}_2\text{O}] + k_{12} [\text{O}_2] [\text{M}])$$

The quantity δ can be computed since at room temperature $k_{10} = 1.26 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $k_{11} = 5.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ and $k_{12} = 5.5 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ [15]. The values of δ for each run are listed in Table 1.

Equation (IV) indicates a time dependence on the CO growth rate contrary to observation. Therefore, either the second term on the right-hand side of eqn. (IV) is negligible in comparison with the first term or $\exp(-k_{17}t)$ is negligible. The CO quantum yields are not constant and do in fact depend on the $[\text{NO}]/[\text{NO}_2]$ ratio. Thus the exponential term must be negligible and the heterogeneous decay of HO_2NO_2 via reaction (17) must be fast, relative to the reaction times used in this study. This requires $k_{17} \geq 0.1 \text{ min}^{-1}$, a result to be expected from other studies [21] especially since our reaction cell contains gold mirrors which could catalyze the decomposition of HO_2NO_2 .

With the omission of the exponential term, eqn. (IV) can be rearranged to

$$\left\{ \frac{\Phi(\text{CO})}{\xi} - \frac{k_{3a}}{k_3} \right\} \left(1 - \delta \frac{k_{5a}}{k_5} \right) - \frac{k_{3a}}{k_3} - \frac{2\delta k_{3b}}{k_3} = \left(1 + \frac{k_{-13} [\text{M}]}{k_{17}} \right) \frac{k_{14} [\text{NO}]}{k_{13} [\text{NO}_2] [\text{M}]} \quad (\text{VI})$$

The results in Table 1 are at constant total pressure so that the left-hand side of eqn. (VI) can be plotted against the $[\text{NO}]/[\text{NO}_2]$ ratio. This is done in Fig. 4. The data are quite scattered but the logarithmic plot can be fitted by a

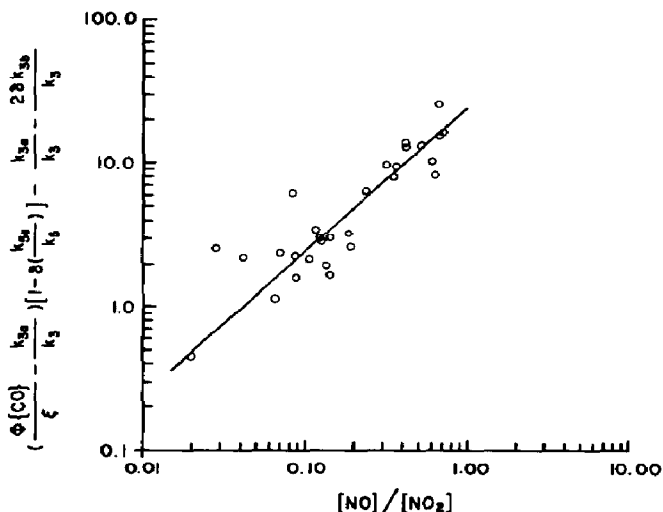


Fig. 4. Logarithmic plot of the left-hand side of eqn. (VI) vs. the $[\text{NO}]/[\text{NO}_2]$ ratio for the data in Table 1. The rate coefficients used to compute the left-hand side of eqn. (VI) were $k_{3a}/k_3 = 0.84$, $k_{3b}/k_3 = 0.16$ and $k_{5a}/k_5 = 0.49$.

straight line of slope 1.0. The scatter is attributed to the fact that the NO concentration is shifting during the reaction so that there is considerable uncertainty in the abscissa values. Nevertheless the intercept gives a value of 24 for $2(1 + k_{-13}[\text{M}]/k_{17})k_{14}/k_{13}[\text{M}]$. If we make the assumption that $1 + k_{-13}[\text{M}]/k_{17} \approx 1$, then $k_{14}/k_{13}[\text{M}] \approx 12$. The accepted value for k_{14} is $8.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [22]. Thus from our data $k_{13}[\text{M}]$ becomes $7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ with 54 Torr O_2 plus 2 Torr CH_2O . This can be compared with the value of $2.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ computed from the low pressure limiting expression for $k_{13} = (15.1 \pm 3.8) \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ found at 300 K with O_2 as a chaperone [23] or with the value of $(2.6 - 3.8) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ found at 283.5 K in the presence of 58 Torr H_2 [24]. Since our value has an uncertainty factor of 2, the comparison can be considered to be acceptable.

In this analysis it was necessary to assume that $k_{-13}[\text{M}]/k_{17} \ll 1$. The value for $k_{-13}[\text{M}]$ can be computed from the data of Graham *et al.* [25] to be 0.012 s^{-1} at 58 Torr equivalent O_2 pressure at 296 K. Thus k_{17} must exceed this value. Simonaitis and Heicklen [21] found a value of 0.0053 s^{-1} for k_{17} in a 2 l Pyrex bulb. Our reaction vessel is an 11 l metal chamber lined with Teflon and containing gold mirrors. Metal surfaces efficiently catalyze peroxide decomposition, so that a value of k_{17} in excess of 0.02 s^{-1} is not unexpected in our system.

That $\exp(-k_{17}t)$ is negligible is also confirmed by the fact that if it is omitted eqn. (V) can be integrated to the empirical form found for the HCOOH growth as given by eqn. (I) with $k_{16} = \tau^{-1} = 1.34 \text{ h}^{-1}$. Thus

$$\Phi(\text{HCOOH})_{\text{eff}}/\xi = (2k_{15}[\text{CH}_2\text{O}]/k_{13}[\text{NO}_2][\text{M}]) (1 + k_{-13}[\text{M}]/k_{17}) \quad (\text{VII})$$

Figure 5 is a logarithmic plot of $\Phi(\text{HCOOH})_{\text{eff}}/\xi$ against the $[\text{CH}_2\text{O}]/[\text{NO}_2]$

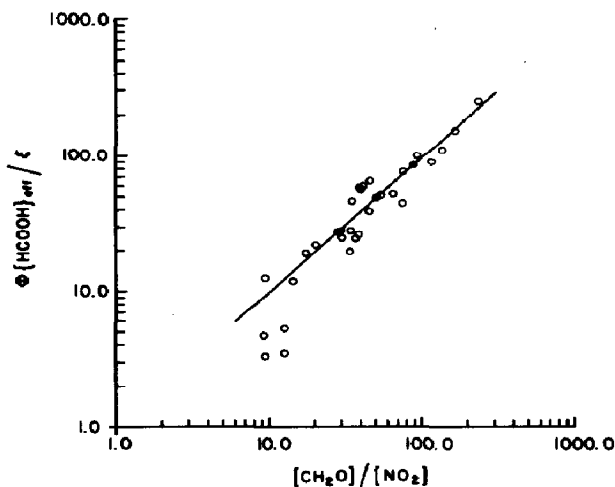
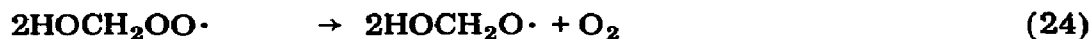
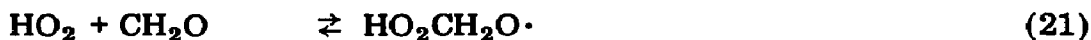


Fig. 5. Logarithmic plot of $\Phi(\text{HCOOH})_{\text{eff}}/\xi$ vs. the $[\text{CH}_2\text{O}]/[\text{NO}_2]$ ratio for the data in Table 1.

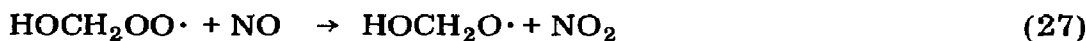
ratio. Except at the low values of this ratio, where little HCOOH is produced and the data are badly scattered, the data are well fitted by a line of slope 1.0, since $1 + k_{-13}[\text{M}]/k_{17} \approx 1$. The intercept gives $2k_{15}/k_{13}[\text{M}] = 0.96$ with an uncertainty factor of about 2. For $k_{13}[\text{M}] \approx 2.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 54 Torr [23, 24], k_{15} becomes about $1.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, approximately a factor of 14 greater than the value reported by Su *et al.* [8]. This value of 0.96 for $2(1 + k_{-13}[\text{M}]/k_{17})k_{15}/k_{13}[\text{M}]$ also can be combined with the value of $2(1 + k_{-13}[\text{M}]/k_{17})k_{14}/k_{13}[\text{M}] = 24$ obtained earlier to give $k_{15}/k_{14} = 25$. Since $k_{14} = 8.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ this gives $k_{15} = 3.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, 32 times greater than the estimate of 1×10^{-14} reported by Su *et al.* [8]. There is considerable uncertainty in both the value of $(1.4 - 3.2) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for k_{15} that we obtained and the value of $1.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ obtained by Su *et al.* [8], yet it is difficult to believe that the discrepancy could encompass a factor of between 14 and 32. The large discrepancy suggests a difference in mechanism.

The mechanism for HO_2 addition to CH_2O proposed by Su *et al.* [8] is



Thus HCOOH is formed from $\text{HOCH}_2\text{OO} \cdot$ via the radical-radical reactions (23) and (24). For Su *et al.* [8] to evaluate k_{15} it was necessary for them to evaluate the equilibrium constant product $K_{21}K_{22}$. Any error in this estimation would give rise to an error in k_{15} and this might account for the discrepancy between our value of k_{15} and that of Su *et al.* [8].

Under our conditions, in which oxides of nitrogen are present, radical-radical reactions are not possible. The fate of the $\text{HOCH}_2\text{OO}\cdot$ radical should be



with reaction (27) followed by reaction (25). However, this mechanism leads to an inconsistency with our observations. If the equilibrium in reaction (26) is rapidly established, as it should be, then the rate laws can be derived by substituting reactions (21), (22), (25), (26), (-26) and (27) for reactions (15) and (16). The resulting rate laws are essentially those given in eqns. (IV) and (V) but there is no term that contains k_{16} :

$$\frac{d[\text{HCOOH}]}{dt} = 2\xi I_a \frac{k_{21}[\text{CH}_2\text{O}]}{k_{13}[\text{NO}_2][\text{M}]} \left[1 + \frac{k_{-13}[\text{M}]}{k_{17}} \{1 - \exp(-k_{17}t)\} \right] \quad (\text{VIII})$$

$$\begin{aligned} \frac{d[\text{CO}]}{dt} = & \left(\frac{k_{3a}}{k_3} + \frac{k_{3a}/k_3 + 2\delta k_{3b}/k_3}{1 - \delta k_{5a}/k_5} \right) \xi I_a + \\ & + \frac{2\xi I_a k_{14}[\text{NO}]}{(1 - \delta k_{5a}/k_5) k_{13}[\text{NO}_2][\text{M}]} \left[1 + \frac{k_{-13}[\text{M}]}{k_{17}} \{1 - \exp(-k_{17}t)\} \right] \end{aligned} \quad (\text{IX})$$

The HCOOH data can be fitted nicely to the expression in eqn. (VIII). However, the best fit to the data arises when $k_{17} = 1.0 \text{ h}^{-1}$. This is much smaller than the value expected from the observations of others [21]. The CO rate law requires that there be some curvature to the growth plots. While the CO data are not unambiguous, there appeared to be no marked curvature in the [CO] against time plots. If we try to model this system, the calculated CO pressures are significantly larger than the measured pressures. If reaction (-26) is quite slow, then the HCOOH data would depend on the $[\text{NO}]/[\text{NO}_2]$ ratio. This is clearly in conflict with our results and thus this assumption must be incorrect.

Table 3 is a summary of the rate coefficient data obtained in this study. Our conclusion is that the mechanism of HCOOH formation in our system is not resolved and that the rate coefficient data regarding it must be accepted with reservation. However, the values of the rate coefficient ratios k_{3b}/k_3 and k_9/k_{7a} should be meaningful, since the analysis for them is independent of the mechanism of HCOOH formation.

Acknowledgments

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TABLE 3

Summary of rate coefficient data

Rate coefficient	Value	Units	Reference
k_{3b}/k_3	$< 0.16 \pm 0.02$ ≈ 0.30	None None	This work 12
k_{13}	$\approx 7 \times 10^{-13}$ ^a $(2.8 \pm 0.7) \times 10^{-13}$ ^b $(2.6 - 3.8) \times 10^{-13}$ ^c	$\text{cm}^3 \text{s}^{-1}$ $\text{cm}^3 \text{s}^{-1}$ $\text{cm}^3 \text{s}^{-1}$	This work 23 24
k_9/k_{7a}	0.21 ± 0.07 ^d	None	This work
k_{15}	$(1.4 - 3.2) \times 10^{-13}$ $\approx 1.0 \times 10^{-14}$	$\text{cm}^3 \text{s}^{-1}$ $\text{cm}^3 \text{s}^{-1}$	This work 8
k_{16}	1.34	h^{-1}	This work

^a At 54 Torr O₂ plus 2 Torr CH₂O. There is an uncertainty factor of 2.

^b At 58 Torr O₂.

^c At 58 Torr H₂.

^d k_9/k_{7a} could be as high as 0.63 if $k_{5a}/k_5 = 0$, rather than the value of 0.49 reported earlier [9].

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