

THE REACTIONS OF HO WITH CH₂O AND OF HCO WITH NO₂

BOYCE M. MORRISON, JR., and JULIAN HEICKLEN

Department of Chemistry, Ionosphere Research Laboratory and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pa., 16802 (U.S.A.)

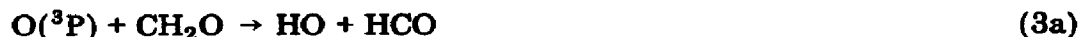
(Received September 17, 1979; in revised form December 11, 1979)

Summary

NO₂ was photolyzed at 366 nm in the presence of CH₂O at 296 K. Products of the reaction were CO and CO₂. H₂, HCOOH and N₂O were not produced. The results establish that the reaction of HO with CH₂O does not produce HCOOH, but there is evidence that about 50% of the HCO produced has sufficient excess energy to decompose spontaneously to H and CO. The reaction of HCO with NO₂ has two major (and probably exclusive) pathways:



with $k_{9c}/k_{9e} \approx 1.14 \pm 0.13$ if $k_{3b}/k_3 = 0$, or $k_{9c}/k_{9e} \approx 0.99 \pm 0.13$ if $k_{3b}/k_3 \approx 0.30$, where reactions (3) are



1. Introduction

Formaldehyde is present in polluted urban atmospheres and a complete understanding of its photooxidation is essential. There have been many recent studies involving the photooxidation of formaldehyde [1 - 5]. Formic acid has been observed as a product of CH₂O oxidation [1, 4 - 9]. Several reactions have been postulated to explain its production. They include the reaction of HCO with O₂ [1], the reaction of O₂ with electronically excited CH₂O or its isomer H $\dot{\text{C}}$ OH [4], and the reactions of HO and HO₂ with CH₂O [2, 5, 9].

A main purpose of this study was to determine whether HO could react with CH₂O to produce HCOOH directly. To do this HO was generated by photolyzing NO₂ to produce O(³P) atoms in the presence of CH₂O. The O(³P) atoms abstracted a hydrogen atom from CH₂O to produce HO and

HCO. Thus we were also able to study the reactions of HCO with NO_2 to determine the importance of the various product pathways.

The thermal reaction of CH_2O and NO_2 was first studied by Pollard and Wyatt [10] and Pollard and Woodward [11]. In their work they found that CO and CO_2 were produced in a ratio of about 3:2 at 154 °C [10] for a 2:1 $[\text{CH}_2\text{O}]/[\text{NO}_2]$ ratio. This value increased slightly with temperature. They found no evidence for HCOOH production. They proposed that an intermediate $\text{CH}_2\text{O}\cdot\text{NO}_2$ reacted with NO_2 to produce CO and CO_2 . Thomas [12] has studied the thermal oxidation of glyoxal by NO_2 at 160 - 210 °C. In his article the results of Pollard and Wyatt [10] were explained by a different mechanism than the one originally proposed. This new mechanism included the reaction of HCO with NO_2 to give the observed products, CO and CO_2 , in a constant ratio.

Barton [13] has investigated the thermal oxidation of the various deuterated isotopes of formaldehyde with NO_2 at 126 °C and has found that the ratio of CO to CO_2 produced decreased as the $[\text{NO}]/[\text{CH}_2\text{O}]$ ratio increased above unity. He concluded "that (a) some fraction of the CO is formed from an intermediate without reaction of the intermediate with NO_2 and (b) H abstraction is more important in the reaction controlling the rate of formation of CO than in the reaction controlling the rate of formation of CO_2 ."

2. Experimental

The experimental apparatus and the purification of CH_2O and helium have been described previously [4]. The reaction vessel was a long-path IR cell vertically mounted in a Beckman model 10 IR spectrophotometer. Thus HCOOH production and NO_2 decay could be monitored continuously by IR absorption spectroscopy during photolysis. The gases CO, CO_2 , H_2 and N_2O were measured by gas chromatography after the photolysis had been terminated.

A Corning O-52 filter was used to cut off radiation below 340 nm. This allowed the NO_2 molecule to absorb radiation from the 366 nm line produced by a Hanovia 140 W medium pressure mercury lamp. At this wavelength no CO, CO_2 or H_2 were observed when pure CH_2O was irradiated. The quantum yield for the removal of NO_2 in the absence of any added gases was taken to be 2. Actinometry was performed by monitoring the decay of the NO_2 absorbance as a function of time.

The absorbance of NO_2 was measured in two different ways during this study. Initially the IR spectrum of the mixture was taken at several intervals during a reaction. The absorbance and hence the pressure of NO_2 could be determined from the spectrum. Subsequently an external recorder was connected to the IR spectrophotometer. This allowed the absorbance of NO_2 to be monitored continuously during an experiment. In this way more accurate pressures of NO_2 could be determined.

NO_2 was purified by mixing 100 Torr of NO_2 with 600 Torr O_2 . The mixture was frozen at -196°C and then warmed to room temperature. This procedure was repeated until the blue color of N_2O_3 had disappeared and the frozen mixture was white. The NO_2 was then distilled from -63 to -130°C .

3. Results

NO_2 was photolyzed at 296 K with 366 nm radiation in the presence of CH_2O and in the presence of CH_2O and helium. The CH_2O pressure was varied from 0.020 Torr to 5.62 Torr and the NO_2 pressure ranged from 21.9 mTorr to 388 mTorr. One series of reactions was performed at a constant $\text{CH}_2\text{O}:\text{NO}_2$ pressure ratio with the helium pressure varying from 45 Torr to 750 Torr. In the dark no products formed, but the CH_2O disappeared slowly by polymerization. Also NO_2 was present only as the monomer and no change in NO_2 absorbance was observed.

The products measured were CO and CO_2 . The loss of NO_2 was also measured. Compounds not produced were H_2 , HCOOH and N_2O . These compounds would have been detected at quantum yields greater than 0.08, 0.10 and 0.06 respectively. From the absence of N_2O it was concluded that no HNO was produced. N_2O would have arisen from the reaction of HNO with itself. Because NO was difficult to analyze, its quantum yield was not determined for any of the experiments. In experiments with high NO_2 and high CH_2O pressures, a broad band between 700 and 800 cm^{-1} grew in the IR spectrum. This is the region of nitrite and nitrate absorption. The band is therefore tentatively assigned to a compound with the formula HC(O)NO_2 or HC(O)ONO .

Tables 1 and 2 give the quantum yields for CO and CO_2 production and for NO_2 removal under various initial conditions. The quantities of interest for CO and CO_2 are the measured quantum yields divided by the quantity ξ , which is the fraction of $\text{O}(^3\text{P})$ atoms that react with CH_2O . The adjusted quantum yields are scattered about a mean value for most of the conditions used in these experiments. Figure 1 is a plot of $\Phi(\text{CO})/\xi$ versus $\log([\text{CH}_2\text{O}]/[\text{NO}_2])$. The average value for $\Phi(\text{CO})/\xi$ is 3.12 ± 0.53 (1σ). Figure 2 is a plot of $\Phi(\text{CO}_2)/\xi$ versus $\log([\text{CH}_2\text{O}]/[\text{NO}_2])$. The mean value is 2.28 ± 0.25 (1σ). When NO_2 is in excess of CH_2O , the adjusted quantum yields of CO and CO_2 are not in agreement with the average value. The small amounts of CO and CO_2 produced under these conditions lead to large errors in measurement and the deviations are not considered meaningful.

The average value for $\Phi(\text{CO})/\Phi(\text{CO}_2)$ of $1.37_{0.35}^{0.27}$ is in good agreement with the values found by Pollard and Wyatt [10] at higher temperatures. In fact Shaw [14] has shown that the data of Pollard and Wyatt give an activation energy of 650 cal mol^{-1} for the ratio. Thus, at 296 K their ratio would extrapolate to 1.07 which agrees with our value within experimental uncertainty.

TABLE 1

The photolysis of NO_2 at 366 nm in the presence of CH_2O

$\frac{[\text{CH}_2\text{O}]}{[\text{NO}_2]}$	$[\text{NO}_2]$ (mTorr)	$[\text{CH}_2\text{O}]$ (Torr)	Irradiation time (h)	I_a (mTorr h ⁻¹)	$\Phi(\text{CO})$	$\Phi(\text{CO}_2)$	$-\Phi(\text{NO}_2)$	ξ	$\frac{\Phi(\text{CO})}{\xi}$	$\frac{\Phi(\text{CO}_2)}{\xi}$	$-\frac{\Phi(\text{NO}_2) - 2 + \xi}{\xi}$
0.063	300	0.020	4.5	4.38	<0.015	<0.065	1.62	0.0011	<13.6	<59	—
0.159	302	0.048	4.75	4.41	0.020	0.021	1.67	0.0026	7.69	8.08	—
0.348	302	0.105	4.0	4.41	<0.023	0.063	1.93	0.0057	<4.04	11.1	—
0.502	301	0.151	4.25	4.40	<0.010	0.047	2.35	0.0081	<1.16	5.80	43.8
0.695	295	0.205	4.25	4.30	<0.028	0.069	2.26	0.0113	<2.49	6.11	24.0
0.958	309	0.296	4.0	4.52	<0.010	0.062	2.56	0.0154	<0.61	4.03	37.4
1.03	282	0.290	4.0	4.10	<0.010	0.095	2.03	0.0166	<0.63	5.72	2.8
1.64	303	0.497	4.0	4.43	0.036	0.059	2.26	0.0262	1.38	2.25	10.9
1.70	305	0.518	4.0	4.46	0.101	0.062	2.31	0.0271	3.73	2.27	12.4
2.50	294	0.736	4.0	4.29	0.087	0.100	2.71	0.0394	2.22	2.53	19.0
2.62	297	0.777	4.0	4.33	0.130	0.100	3.32	0.0411	3.16	2.43	33.0
3.12	309	0.964	4.0	4.52	0.135	0.114	3.20	0.0486	2.79	2.35	25.7
3.18	153	0.486	6.0	2.06	0.143	0.125	2.43	0.0494	2.89	2.53	9.7
3.34	317	1.06	4.0	4.65	0.187	0.126	3.50	0.0519	3.60	2.43	30.0
4.82	104	0.501	4.0	1.28	0.216	0.176	4.12	0.0731	2.95	2.41	17.5
4.94	102	0.504	4.0	1.25	—	0.126	2.90	0.0748	—	1.68	13.0
5.08	388	1.97	5.5	5.77	0.330	0.206	3.88	0.0768	3.71	2.32	22.1
5.51	303	1.67	5.1	4.43	0.174	0.159	3.61	0.0828	2.10	1.92	20.4
6.29	205	1.29	5.0	2.88	0.200	0.221	2.89	0.0934	2.14	2.37	10.5
6.99	246	1.72	5.0	3.53	0.260	0.201	2.88	0.103	2.52	1.95	9.5
8.35	303	2.53	4.0	4.43	0.361	0.245	4.74	0.120	3.01	2.04	23.8
9.53	50.9	0.485	4.0	0.444	0.421	0.326	4.32	0.135	3.12	2.41	18.2
9.55	52.9	0.505	6.0	0.476	0.300	0.475	2.80	0.135	2.22	3.52	6.9
9.77	53.3	0.521	4.0	0.482	0.350	0.410	3.00	0.138	2.54	2.97	8.2
10.1	48.9	0.493	6.0	0.413	0.147	0.394	3.80	0.142	1.04	2.77	13.6
10.5	45.9	0.483	4.0	0.388	0.541	0.376	4.41	0.147	3.68	2.56	17.4
11.7	133	1.56	5.0	1.72	0.378	0.335	3.79	0.161	2.35	2.08	12.1
15.0	118	1.77	5.0	1.54	0.480	0.433	4.14	0.197	2.44	2.20	11.9
15.7	98.7	1.55	5.0	1.20	0.537	0.480	3.80	0.205	3.01	2.34	9.8
16.4	297	4.86	4.0	4.33	0.684	0.412	—	0.211	3.24	1.95	—

22.1	77.8	1.72	6.0	0.869	0.798	0.634	4.54	0.266	3.00	2.38	10.5
28.4	54.9	1.56	6.0	0.507	1.05	0.844	5.50	0.318	3.30	2.65	12.0
30.9	158	4.88	5.0	2.14	1.05	0.565	4.78	0.336	3.13	1.68	9.3
32.8	156	5.12	6.1	2.10	1.21	0.695	4.70	0.350	3.46	1.99	8.7
33.4	152	5.08	5.0	2.04	1.18	0.751	4.50	0.354	3.33	2.12	8.1
41.4	38.9	1.61	6.5	0.355	1.42	0.902	8.19	0.404	3.51	2.23	16.3
49.6	102	5.06	5.0	1.25	1.43	0.835	5.36	0.448	3.19	1.86	8.5
53.0	24.9	1.32	4.0	0.247	1.67	1.30	7.04	0.478	3.49	2.72	11.5
55.3	32.9	1.82	4.0	0.326	1.79	1.15	5.37	0.475	3.77	2.42	8.1
71.9	24.9	1.79	6.0	0.247	0.665	1.16	6.40	0.540	1.23	2.15	9.1
78.1	21.9	1.71	3.0	0.217	0.500	1.73	6.31	0.562	0.891	3.08	8.7
79.9	23.9	1.91	3.0	0.237	—	1.76	6.12	0.567	—	3.10	8.3
95.4	53.9	5.14	6.0	0.492	2.91	1.39	8.10	0.610	4.77	2.28	11.0
97.7	55.9	5.46	5.0	0.523	2.41	1.11	6.83	0.615	3.92	1.80	8.8
99.8	53.9	5.38	5.0	0.492	3.01	1.50	8.40	0.620	4.85	2.42	11.0
103	47.9	4.91	5.0	0.397	1.94	1.64	8.93	0.627	3.09	2.62	12.1

TABLE 2

The effect of total pressure on the photolysis of NO_2 at 366 nm in the presence of CH_2O

[He] (Torr)	$\frac{[\text{CH}_2\text{O}]}{[\text{NO}_2]}$	$[\text{NO}_2]$ (mTorr)	$[\text{CH}_2\text{O}]$ (Torr)	Irradiation time (h)	I_a (mTorr h ⁻¹)	$\Phi(\text{CO})$	$\Phi(\text{CO}_2)$	$-\Phi(\text{NO}_2)$	ξ	$\frac{\Phi(\text{CO})}{\xi}$	$\frac{\Phi(\text{CO}_2)}{\xi}$	$\frac{-\Phi(\text{NO}_2) - 2 + \xi}{\xi}$
44.5	92.4	53.9	4.98	6.0	0.492	2.30	1.53	6.0	0.610	3.77	2.51	7.6
95.0	93.6	52.9	4.95	6.0	0.476	1.54	1.32	8.6	0.605	2.55	2.19	12.0
145	91.1	53.9	4.91	6.0	0.492	2.24	1.46	9.1	0.599	3.73	2.44	13.0
200	93.6	54.9	5.14	8.0	0.507	2.15	1.26	7.9	0.605	3.56	2.08	11.0
250	110	50.9	5.62	6.0	0.444	2.48	1.23	8.1	0.643	3.85	1.92	10.0
300	96.1	51.9	4.99	5.0	0.460	2.01	1.13	8.4	0.612	3.28	1.85	11.0
400	87.1	55.9	4.87	6.0	0.523	1.95	1.41	5.5	0.588	3.32	2.40	9.4
600	95.1	52.9	5.03	6.0	0.476	2.10	1.45	6.9	0.609	3.45	2.38	9.1
750	88.3	57.3	5.06	6.0	0.545	1.69	1.20	10.0	0.591	2.86	2.03	14.0

The removal quantum yields of NO_2 are adjusted in a slightly different manner than those for $\Phi(\text{CO})$ or $\Phi(\text{CO}_2)$ (see Section 4). The adjusted expression is $\{-\Phi(\text{NO}_2) - 2 + \xi\}/\xi$ and represents the NO_2 loss as a result of the reaction of $\text{O}(^3\text{P})$ atoms with CH_2O . These adjusted values are constant for a $[\text{CH}_2\text{O}]/[\text{NO}_2]$ ratio between 10 and 100. Below a value of 10 the adjusted quantum yield tends to have more scatter, since $-\Phi(\text{NO}_2)$ is close to $2 - \xi$ and the difference has a large percentage uncertainty. Figure 3 is a plot of $\{-\Phi(\text{NO}_2) - 2 + \xi\}/\xi$ versus $\log([\text{CH}_2\text{O}]/[\text{NO}_2])$. The mean value for $\{-\Phi(\text{NO}_2) - 2 + \xi\}/\xi$ is 10.4 ± 1.8 (1σ). The mean values for the adjusted quantum yields are summarized in Table 3.

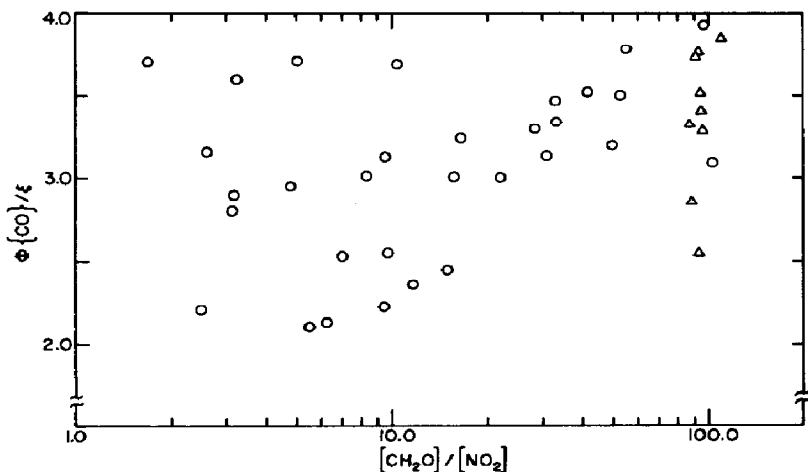


Fig. 1. A semilogarithmic plot of $\Phi(\text{CO})/\xi$ vs. $[\text{CH}_2\text{O}]/[\text{NO}_2]$: \circ , helium absent; \triangle , helium present.

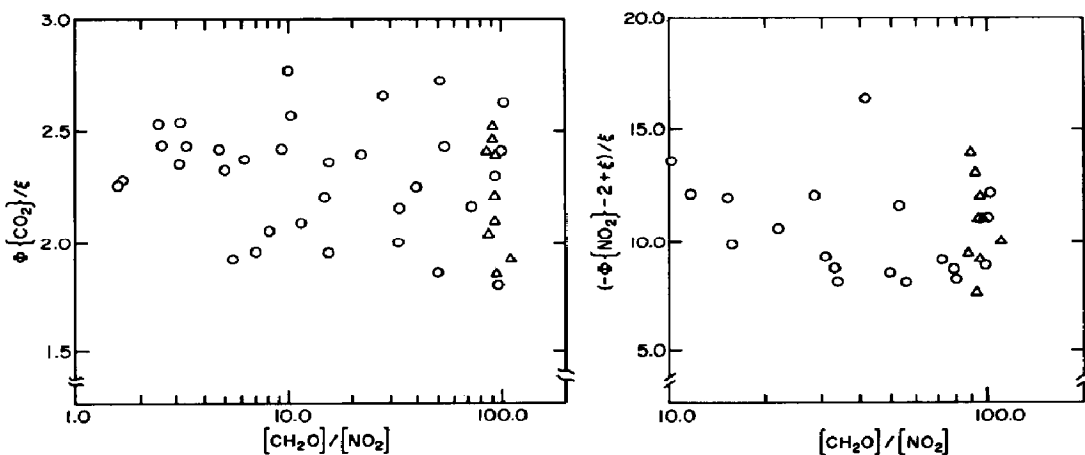


Fig. 2. A semilogarithmic plot of $\Phi(\text{CO}_2)/\xi$ vs. $[\text{CH}_2\text{O}]/[\text{NO}_2]$: \circ , helium absent; \triangle , helium present.

Fig. 3. A semilogarithmic plot of $\{-\Phi(\text{NO}_2) - 2 + \xi\}/\xi$ vs. $[\text{CH}_2\text{O}]/[\text{NO}_2]$: \circ , helium absent; \triangle , helium present.

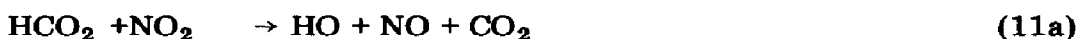
TABLE 3
Summary of findings

<i>Function</i>	<i>Value</i>	<i>Units</i>
$\Phi(\text{CO})/\xi$	3.12 ± 0.53	None
$\Phi(\text{CO}_2)/\xi$	2.28 ± 0.25	None
$\{-\Phi(\text{NO}_2) - 2 + \xi\}/\xi$	10.4 ± 1.8	None

4. Discussion

The $\text{O}(^3\text{P})$ atoms generated in the photolysis of NO_2 react with both NO_2 and CH_2O . Those which react with CH_2O generate a chain reaction. The complete mechanism is given as follows. Most of the reactions are those postulated by earlier workers [2, 12].





Here HCO^\ddagger is a vibrationally excited radical with enough energy to decompose spontaneously. Horowitz *et al.* [2] have given evidence that such a species is produced in the reaction of HO with CH_2O .

The complete mechanism leads to very complex rate laws. Fortunately, however, many simplifications can be made. As previously stated, one of the main purposes of this study was to determine whether HO could react with CH_2O to produce HCOOH . The absence of HCOOH as a product eliminates reaction (4c). Likewise the absence of N_2O as a product eliminates reactions (9d) and (12). Finally the failure to detect H_2 eliminates reaction (8) as being important in this system. Reaction (8) is known to occur with a rate coefficient of $5.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 297 K [15]. However, this reaction is too slow to compete with reaction (7) in our experiments since $k_7 = 1.13 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 298 K [15]. Thus even under the most favorable conditions for reaction (8), *i.e.* when $[\text{CH}_2\text{O}]/[\text{NO}_2] = 110$, reaction (8) removes less than 0.05% of the hydrogen atoms.

Reactions (6) and (13) can be eliminated because there is no effect of adding even an atmosphere of helium. Thus if HCO^\ddagger is produced at all it decomposes 100% in our system. Further evidence that reaction (13) is unimportant comes from a comparison of rate coefficients. Since $k_4 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 296 K [15] and $k_{13} = 8.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ in the presence of helium at 296 K [15], then even under the most favorable conditions, *i.e.* high [M] and low $[\text{CH}_2\text{O}]/[\text{NO}_2]$, reaction (13) accounts for less than 1.8% of the removal of HO atoms. Thus if reaction (13) was the important terminating step, then the adjusted quantum yields would exceed 56, contrary to observation. Consequently reaction (13) can be neglected.

Reactions (11) have not been postulated previously since HCO_2 is believed to be unstable, as are the analogous RCO_2 radicals. If reactions (11b) or (11c) occur, then reactions (11) must occur to the exclusion of reaction (10), since the results are independent of $[\text{CH}_2\text{O}]/[\text{NO}_2]$. (If only reaction (11a) occurs it makes no difference, since reaction (11a) is then kinetically indistinguishable from reaction (10) followed by reaction (7).) Thus even at 20 mTorr NO_2 , reactions (11), if they occur, must dominate reaction (10). Since k_{11} cannot exceed $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and probably would be at

least an order of magnitude smaller, k_{10} must be less than $1.3 \times 10^5 \text{ s}^{-1}$. The pre-exponential factor for k_{10} should exceed 10^{16} s^{-1} , so that the activation energy required would be greater than $14.7 \text{ kcal mol}^{-1}$, which would have to be less than the H-CO₂ bond dissociation energy. This is extremely unlikely and it can be concluded that reactions (11) are of no importance.

The only evidence for reaction (3b) is a recent finding [16] that it accounts for approximately 30% of the total reaction. It, and reaction (9c) followed by reaction (10), are the only sources of CO₂.

Application of the steady state hypothesis on O(³P), HO, HCO[±], HCO, H and HCO₂ to the simplified mechanism consisting of reactions (1), (2), (3a), (3b), (4a), (4b), (5), (7), (9a), (9b), (9c), (9e) and (10) leads to the following rate laws:

$$\Phi(\text{CO}_2)/\xi = k_{3b}/k_3 + 2k_{9c}/(k_{9b} + k_{9e}) \quad (\text{I})$$

$$\Phi(\text{CO})/\xi = \frac{2(k_{9a} + k_{9b})}{(k_{9b} + k_{9e})} + \frac{k_{4a}}{k_{4b}} \left\{ 1 + \frac{k_{3b}}{k_3} + \frac{2(k_{9a} + k_{9c})}{(k_{9b} + k_{9e})} \right\} \quad (\text{II})$$

$$\frac{\{-\Phi(\text{NO}_2) - 2 + \xi\}}{\xi} = \frac{2k_{3b}}{k_3} + \frac{2(k_9 + k_{9c})}{k_{9b} + k_{9e}} + \frac{k_{4a}}{k_{4b}} \left\{ 1 + \frac{k_{3b}}{k_3} + \frac{2(k_{9a} + k_{9c})}{(k_{9b} + k_{9e})} \right\} \quad (\text{III})$$

where ξ is the fraction of O(³P) atoms that react with CH₂O and is defined by

$$\xi \equiv k_3 [\text{CH}_2\text{O}] / (k_2 [\text{NO}_2] + k_3 [\text{CH}_2\text{O}])$$

Thus the left-hand sides of eqns. (I) - (III) represent the adjusted quantum yields resulting only from the reactions of O(³P) with CH₂O. CO₂ and CO can only be produced via these reactions (reactions (3)) but, for NO₂ removal, corrections for loss due to reactions (1) and (2) have to be taken into account. The quantity ξ can be computed for each run from the known rate coefficients which are $k_2 = 9.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $k_3 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at room temperature [15].

Equations (I) - (III) can be combined to give the following simpler and more useful expression:

$$\begin{aligned} \phi &\equiv \{-\Phi(\text{NO}_2) - 2 + \xi - 2\Phi(\text{CO}_2) - \Phi(\text{CO})\}/\xi \\ &= 2k_{9e}/(k_{9b} + k_{9e}) \end{aligned} \quad (\text{IV})$$

The magnitude of ϕ is 2.72 ± 2.03 where the uncertainty is the sum of the uncertainties for $\{-\Phi(\text{NO}_2) - 2 + \xi\}/\xi$, $\Phi(\text{CO})/\xi$ and twice that for $\Phi(\text{CO}_2)/\xi$. Thus the uncertainty is grossly exaggerated. Since $2k_{9e}/(k_{9b} + k_{9e})$ cannot exceed 2.0 and since ϕ is not likely to be very much below 2.0, it can be concluded that reaction (9b) is unimportant and that reaction (9e) is the important terminating reaction.

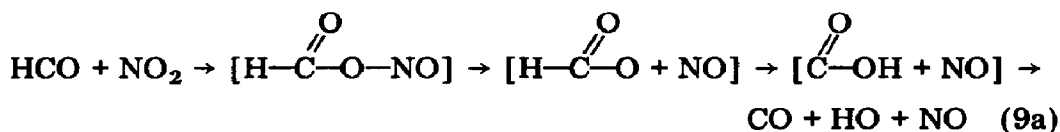
Equations (I) and (II) now reduce to

$$\Phi(\text{CO}_2)/\xi = 2.28 \pm 0.25 = k_{3b}/k_3 + 2k_{9c}/k_{9e} \quad (\text{V})$$

$$\Phi(\text{CO})/\xi = 3.12 \pm 0.53 = \frac{2k_{9a}}{k_{9e}} + \frac{k_{4a}}{k_{4b}} \left\{ 1 + \frac{k_{3b}}{k_3} + \frac{2(k_{9a} + k_{9c})}{k_{9e}} \right\} \quad (\text{VI})$$

Since k_{3b}/k_3 cannot exceed 1.0, and in fact is either 0 or approximately 0.30, then reaction (9c) must be an important chain-propagating step and is the main source of CO_2 in our system. Furthermore $k_{9c}/k_{9e} = 1.14 \pm 0.13$ if $k_{3b}/k_3 = 0$ or $k_{9c}/k_{9e} \approx 0.99 \pm 0.13$ if $k_{3b}/k_3 \approx 0.30$.

A compound with the formula HC(O)NO_2 or HC(O)ONO has been postulated as a product in the chain-terminating reaction (9e). Topchiev *et al.* [17] have predicted that reaction (9) has two pathways. One is reaction (9c) followed by reaction (10). The other, which they felt would be dominant, is equivalent to reaction (9a) but proceeds through reaction (9e):



Because their experiments were performed at about 700 K, any intermediate compound may not have been stable. At room temperature the compound HC(O)NO_2 or HC(O)ONO may be stable enough to exist in the system studied in this work. The work of Pollard and coworkers [10, 11], Thomas [12] and Barton [13] was carried out at elevated temperatures. None of these workers has reported the existence of HC(O)NO_2 or HC(O)ONO .

The CO must arise either from reaction (4a) or (9a) or from both. The results obtained here cannot distinguish amongst the possibilities, but there are other arguments which tend to favor reaction (4a) as being the important CO-producing step. These are the following.

(1) Reaction (9a) should not be important when reaction (9b) is not important, since both reactions have the same activated complex and reaction (9b) is energetically more favorable.

(2) Reactions (9a) and (9b) are unlikely since they require that NO_2 must react with the hydrogen atom of HCO rather than with the radical site on the carbon atom. Reactions (9c) and (9e), both of which do occur, involve reaction at the radical site. The similar reaction of HO_2 with NO_2 occurs only at the radical site of HO_2 and does not lead to hydrogen atom abstraction [18].

(3) There is evidence from the work of Horowitz *et al.* [2] that HCO^\ddagger is produced by the reaction of HO with CH_2O and that it dissociates spontaneously.

(4) Barton [13] has concluded that, in the thermal reaction between NO_2 and CH_2O , at least some of the CO must be produced in a reaction not involving NO_2 .

If we make the likely assumption, based on these arguments, that reaction (9a) is negligible, then eqns. (V) and (VI) combine to give

$$\Phi(\text{CO})/\xi = (k_{4a}/k_{4b})\{1 + \Phi(\text{CO}_2)/\xi\} \quad (\text{VII})$$

so that $k_{4a}/k_4 = 0.49^{+0.16}_{-0.13}$. This value is the upper limit that can be obtained from our data, but it is smaller than that reported by Horowitz *et al.* [2] who concluded that reaction (4a) was much more important than reaction (4b). However, their analysis may be questioned since they also concluded that reaction (4c) was important.

Acknowledgments

This work was supported by the National Science Foundation (through Grant No. ATM 76-83378) and by the Center for Air Environment Studies to whom we are grateful.

References

- 1 T. L. Osif and J. Heicklen, *J. Phys. Chem.*, **80** (1976) 1526.
- 2 A. Horowitz, F. Su and J. G. Calvert, *Int. J. Chem. Kinet.*, **10** (1978) 1099.
- 3 G. K. Moortgat and P. Warneck, *J. Chem. Phys.*, **70** (1979) 3639.
- 4 B. M. Morrison, Jr., and J. Heicklen, *J. Photochem.*, **11** (1979) 183.
- 5 F. Su, J. G. Calvert and J. H. Shaw, *J. Phys. Chem.*, **83** (1979) 3185.
- 6 J. E. Carruthers and R. G. W. Norrish, *J. Chem. Soc.*, (1936) 1036.
- 7 E. C. A. Horner and D. W. G. Style, *Trans. Faraday Soc.*, **50** (1954) 1197.
- 8 E. C. A. Horner, D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **50** (1954) 1201.
- 9 F. Su, J. G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage and R. D. Breitenbach, *Chem. Phys. Lett.*, **65** (1979) 221.
- 10 F. H. Pollard and R. M. H. Wyatt, *Trans. Faraday Soc.*, **45** (1949) 760.
- 11 F. H. Pollard and P. Woodward, *Trans. Faraday Soc.*, **45** (1949) 767.
- 12 J. H. Thomas, *Trans. Faraday Soc.*, **49** (1953) 630.
- 13 D. Barton, *J. Phys. Chem.*, **65** (1961) 1831.
- 14 R. Shaw, *J. Chem. Soc.*, (1964) 1517.
- 15 R. F. Hampson, Jr., and D. Garvin, Reaction rate and photochemical data for atmospheric chemistry — 1977, *Natl Bur. Stand. (U.S.) Spec. Publ.*, **513** (1977).
- 16 J. S. Chang and J. R. Barker, *J. Phys. Chem.*, **83** (1979) 3059.
- 17 A. V. Topchiev, A. P. Ballod, T. V. Ferdorova and V. Ya. Shtern, *Pet. Chem. USSR*, **2** (1962) 150.
- 18 R. Simonaitis and J. Heicklen, *Int. J. Chem. Kinet.*, **10** (1978) 67.