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THE MERCURY SENSITIZED OXIDATION OF CARBON MONOXIDE

by

R. Simonaitis and Julian Heicklen

June 2, 1971

(Accepted for publication in International Journal of Chemical Kinetics)

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TABLE OF CONTENTS

Abstract	i
INTRODUCTION	1
EXPERIMENTAL	5
RESULTS	7
DISCUSSION	20
REFERENCES	39

ABSTRACT

The mercury-photosensitized oxidation of CO was studied at 275°C over a wide range of $[O_2]/[CO]$ ratios in the absence and presence of the O atom scavenger 2-trifluoromethylpropene (TMP) and at 25°C at low $[O_2]/[CO]$ ratios in the presence of TMP. By following the quantum yield of CO_2 production, $\Phi\{CO_2\}$, as a function of the $[O_2]/[CO]$ ratio, the reactions of vibrationally excited CO ($v \leq 9$) and electronically excited O_2, probably in the $c\,^1\Sigma_u^-$ state, were studied. At low $[O_2]/[CO]$ ratios the predominant reactions are of vibrationally excited CO ($v \leq 9$). Relative rate constants for chemical reaction vs. deactivation of CO ($v \leq 9$) were obtained. At higher $[O_2]/[CO]$ ratios the principal reactions are of electronically excited O_2. Relative rate constants for chemical reactions and deactivation of this electronically excited O_2 with CO, O_2 and TMP were obtained. From the effect of total pressure on $\Phi\{CO_2\}$, it is proposed that an intermediate CO_3 is formed in the reaction of electronically excited O_2 with CO.

INTRODUCTION

Recombination of oxygen atoms will give rise to a number of high lying electronic states of oxygen. Oxygen in the $A^3\Sigma_u^+$ state is known to be present in the earth's upper atmosphere as evidenced from the Herzberg emission bands. It is likely that in the atmosphere the $A^3\Sigma_u^+$ state is produced from the recombination of oxygen atoms. Consequently, it is expected that the $C^3\Delta_u$ and $c^1\Sigma_u^-$ states will also be present, though direct spectroscopic observations cannot be made because emission from these states is forbidden. Electronically excited O_2 may also play a role in the conversion of CO to CO_2 in the atmospheres of Mars and Venus. Thus, a study of the reaction of electronically excited O_2 with various species present in planetary atmospheres is of interest.

The $Hg(^3P)$ sensitization of O_2 produces electronically excited O_2[1, 2]

$$Hg(^3P_1) + O_2 \rightarrow Hg(^1S_o) + O_2^* \qquad (1)$$

$Hg(^3P_1)$ is known to be deactivated to the ground state. The exact state of O_2 is uncertain but it probably is the $c^1\Sigma_u^-$ state.[3] The fact that O_2^* does not react with O_2 to produce O_3 very efficiently excludes the $A^3\Sigma_u^+$ state, but the fact that it does react to some extent excludes the lower states of O_2, the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states. All the transitions between ground-state O_2 and the energetically accessible states are optically forbidden. Mercury sensitization permits the optically spin-forbidden transitions. If this is the only optical selection rule which is relaxed, the $c^1\Sigma_u^-$ state is the only permitted product state.

If $Hg(^3P_o)$ is present, reaction 2 will also occur.

$$Hg(^3P_o) + O_2 \rightarrow Hg(^1S_o) + O_2^* \qquad (2)$$

The mercury is necessarily deactivated to the ^1S_o state, but the state of O_2 produced is not known. However there is no reason to believe that the O_2^* produced in reaction 1 is different from that produced in reaction 2.

CO is also effective in deactivating $Hg(^3P_1)$ and $Hg(^3P_o)$.[4,5] In this case, however, electronic excitation of the CO is not possible, since the energy of the lowest excited electronic state of CO is well above the available energy of 113 kcal/mole. Scheer and Fine[4] suggested that the electronic energy of the mercury is converted almost completely to vibrational energy of the CO by resonant energy transfer producing CO in the v = 20 level.

Karl et al.[5] found that in the irradiation of Hg + CO with 2537 A resonance radiation both the $Hg(^3P_1)$ and $Hg(^3P_o)$ states were present and that both are deactivated by CO to give vibrationally excited CO.

$$Hg(^3P_1) + CO \rightarrow Hg(^1S_o) + CO^\dagger \qquad (3)$$

$$Hg(^3P_o) + CO \rightarrow Hg(^1S_o) + CO^\dagger \qquad (4)$$

By observing the infrared chemiluminescence of CO, they found that the highest vibrational level of CO populated is v = 9 by both $Hg(^3P_1)$ and $Hg(^3P_o)$. A set of rate constants for the vibrational population of CO by $Hg(^3P_1)$ and $Hg(^3P_o)$ relative to the population of the v = 9 level was given. These rate constants are: $k_{v=10} = 0$, $k_{v=9} = 1.00$, $k_{v=8} = 15$, $k_{v=7} = 35$, $k_{v=6} = 43$, $k_{v=5} = 48$, $k_{v=4} = 60$, $k_{v=3} = 70$, $k_{v=2} = 80$. The fact that vibrational levels above v = 9 are not populated indicates that only 47% of the electronic energy of the Hg is converted to vibrational energy of the CO, the rest must appear as translational energy of the Hg atom and translational and rotational energy of the CO. Momentum conservation, however, requires that most of the translational energy be taken up by CO. The CO produced in reaction 3 will possess at the most 53 kcal/mole vibrational energy and at least 52 kcal/mole translational + rotational energy. The CO produced in reaction 4 will have 5.0 kcal/mole less energy since this is the energy difference between the two Hg states.

Earlier evidence indicated that reaction 3 was the major process for deactivating $Hg(^3P_1)$ by CO.[4] However more recent work shows that the major (78%) process is[6]

$$Hg(^3P_1) + CO \rightarrow Hg(^1P_o) + CO(v=1) \qquad (5)$$

The corresponding reaction with O_2 does not occur.[7]

Heicklen and Johnston[2] studied the relative reactivity of O_2^* produced by Hg-sensitization with a number of gases, including O_2 and CO. Their experiments did not distinguish between physical and chemical quenching since products were not analyzed. Volman[1] has examined the reaction of O_2^* with O_2. He found ozone as a product with the quantum yield $\Phi\{O_3\}$ being about 0.03, though higher yields have been reported.[1]

One set of objectives of the present investigation was to: 1) examine the products of the reaction between O_2^* and CO (presumably CO_2), 2) obtain the relative degree of physical vs. chemical quenching of O_2^* by both O_2 and CO, and 3) check the relative quenching efficiency of O_2^* by CO and O_2 by a different method. The reaction between O_2^* and CO may produce the intermediate CO_3, and it was hoped that kinetic evidence for the presence of this species might be obtained for this system. The formation of CO_3 produced by the reaction of $O(^1D)$ + CO_2 has been established.[8]

The second major objective was to see if the CO produced in reactions 3 and 4 would react with O_2. The translational and rotational energy of the CO produced in reactions 3 and 4 probably will be lost in a few collisions in the presence of high [CO] and low [O_2], thus leaving a highly vibrationally excited CO molecule. Thus, this system appeared to be an excellent prototype of a possible bimolecular reaction involving a vibrationally hot, but translationally and rotationally cold, molecule.

In order to prevent the consumption of Hg by O_3 via the reactions

$$O_2^* + O_2 \rightarrow O_3 + O$$

$$M + O + O_2 \rightarrow O_3 + M$$

$$O_3 + Hg \rightarrow HgO + O_2$$

experiments were performed at 275°C at which temperature O_3 is unstable. Another set of experiments was performed in the presence of 2-trifluoromethylpropene (TMP) which was expected to serve as a diagnostic test for the presence of oxygen atoms. The reaction of oxygen atoms with TMP has been investigated by Moss and Jennings[9] and by the present authors.[10] The reaction is a clean addition of oxygen atoms to give the 2-trifluoromethylpropionaldehyde (A) and 2-trifluoromethylpropylene oxide (E) with $\Phi\{A\} = 0.40$ and $\Phi\{E\} = 0.60$ independent of temperature (25° - 275°C) and pressure (> 100 torr). It turned out that in the presence of TMP, experiments could also be performed at room temperature as well, providing the [O_2] to [TMP] ratio was ≤ 5.0.

EXPERIMENTAL

The experiments utilized conventional static photochemical techniques. The reaction vessel was a cylindrical quartz cell 5 cm. in diameter and 10 cm. long, jacketed in a wire-wound aluminum furnace with quartz windows. The temperature was regulated to $\pm 1^{\circ}C$ by a Cole-Parmer Proportio Null Regulator Series V300.

Irradiation was from a Hanovia flat-spiral low-pressure mercury resonance lamp. The radiation passed through a 9-54 Corning filter to remove radiation below 2200A.

The gases were saturated with Hg vapor at room temperature and mixed directly in the cell. The CO was purified by passage over glass beads at $-196^{\circ}C$, degassing at $-196^{\circ}C$, and distillation from a trap immersed in liquid argon ($-186^{\circ}C$) to a trap maintained at $-196^{\circ}C$. The 2-trifluoromethylpropene was obtained from Peninsular ChemResearch Inc., and it was purified by preparative gas chromatography on a 1/4-in. diameter by 20-foot long Porapak Q column operating at $25^{\circ}C$. Gas chromatographic analysis showed no detectable impurities. CF_4 was purified by repeated degassing at $-196^{\circ}C$ and distillation from a trap at $-160^{\circ}C$. Air Products and Chemicals Co. Research grade N_2 was purified by passage over glass beads at $-196^{\circ}C$.

For the experiments at $275^{\circ}C$ the cell contents were removed immediately to minimize the decomposition of the aldehyde product. The CO_2, the 2-trifluoromethylpropionaldehyde, and 2-trifluoromethylpropylene oxide products were analyzed on a 10-foot long column at $38^{\circ}C$ packed with 20% Kel-F oil No. 3 on Chromasorb P.

The actinometry utilized was the mercury sensitized decomposition of N_2O in the presence of TMP in order to scavenge the O atoms.

In this system the rate of N_2 production, $R\{N_2\}$, equals I_a, since $\Phi\{N_2\} = 1.00$.[11] The quantum yields of the epoxide and aldehyde were not measured directly since calibrations for A and E were not made. They are based on $\Phi\{A\} = 0.40$ and $\Phi\{E\} = 0.60$ determined by Moss and Jennings at room temperature.[9] Earlier we have shown[10] that $\Phi\{E\}$ and $\Phi\{A\}$ in the N_2O-TMP system are independent of temperature from 25° - $200^\circ C$, and in this investigation it was shown that the yields are also the same at $275^\circ C$.

RESULTS

When mixtures of O_2 and CO saturated with Hg vapor are irradiated with 2537A resonance radiation at room temperature, the only product observed is CO_2. Presumably ozone is also produced, since the rate of CO_2 formation drops to zero after only a few minutes irradiation due to the formation of HgO. For this reason experiments at room temperature in the absence of TMP could not be performed.

When mixtures of O_2 and CO are irradiated in the presence of TMP at room temperature the products observed are CO_2, 2-trifluoromethylpropyleneoxide (E) and 2-triflurormethylpropionaldehyde (A), and their rates of formation are independent of irradiation time provided $[O_2]/[TMP] \leq 5$. The resuits are presented in Table I. The $[CO]/[O_2]$ ratio was varied from 5.22 to 377. The lower limit was imposed by the conditions that $[O_2]/[TMP] \leq 5$ and $([O_2] + 0.29[CO])/[TMP] > 10$. The former condition insures that no O atoms react with O_2 to give O_3 and the latter condition that < 10% of the excited Hg is quenched by TMP. The upper limit for the $[CO]/[O_2]$ ratio is dictated by the necessity to produce sufficient product for analysis.

Two runs were made in the absence of CO at room temperature to see if CO_2, the aldehyde, and the epoxide are products of the reaction between O_2^* and TMP.

In the presence of CO the product yields, $\Phi\{CO_2\}$, $\Phi\{A\}$, and $\Phi\{E\}$, rise in a regular manner as the $[O_2]/[CO]$ ratio increases from 5.22 to 377. There is considerable scatter in $\Phi\{E\}/\Phi\{A\}$, but the average value, 1.50, is the same as when O atoms produced in the Hg-sensitized decomposition of N_2O react with TMP. $\Phi\{CO_2\}$ is in some runs somewhat greater than $\Phi\{E\} + \Phi\{A\}$. In the absence of CO, the

TABLE I

The Mercury Sensitized Oxidation of CO in the Presence of 2-Trifluoromethylpropene at 25°C[a]

$[O_2]$, torr	[CO], torr	$[O_2]$/[CO]	[TMP], torr	Irradiation time, min.	$\Phi\{CO_2\}$	$\Phi\{E\}$	$\Phi\{A\}$	$\Phi\{E\}+\Phi\{A\}$	$\Phi\{E\}/\Phi\{A\}$
1.35	509	0.00265	0.700	100.0	0.0095	0.0039	0.0024	0.0063	1.62
2.30	611	0.00376	1.20	47.0	0.014	0.0076	0.0047	0.012	1.61
1.80	337	0.00535	1.30	30.0	0.020	0.080	0.054	0.134	1.48
2.40	305	0.00788	0.50	80.0	0.034	-	-	-	-
2.56	310	0.00825	0.45	39.0	0.033	-	-	-	-
2.65	312	0.00850	0.45	10.0	0.038	-	-	-	-
2.22	125	0.0178	1.18	35.0	0.066	0.034	0.019	0.053	1.77
19.4	519	0.0374	2.10	20.0	0.067	0.034	0.024	0.058	1.42
21.2	450	0.0472	4.40	20.0	0.067	0.030	0.023	0.053	1.32
15.4	302	0.0510	3.60	10.0	0.096	0.059	0.043	0.103	1.37
6.60	110	0.0660	1.05	15.0	0.117	0.064	0.046	0.11	1.40
24.0	301	0.0800	.500	10.9	0.086	-	-	-	-
42.5	222	0.192	13.0	10.0	0.081	-	-	-	-
43	-	-	13.0	10.0	0.0058	0.038	0.018	0.056	2.10
43	-	-	13.0	10.0	0.0057	0.036	0.018	0.054	2.00

[a] $I_a = 4.00 \times 10^{-9} \frac{\text{Einsteins}}{\text{cc - min}}$

products are still formed, but their yields, particularly of CO_2, are very small. The contribution to the yield of these products from the reaction of O_2^* with TMP will be negligible for all the runs except for the run with 42.5 torr O_2 where the contribution to $\Phi\{E\}$ and $\Phi\{A\}$ will be large; hence $\Phi\{E\}$ and $\Phi\{A\}$ were not determined for this run.

The results for the Hg-sensitized oxidation of CO at 275°C in the absence of TMP are presented in Table II and in the presence of TMP in Table III. Figure 1 displays the data in graphical form. The only product observed at 275°C in the absence of TMP is CO_2 (in the absence of O_2, no CO_2 is formed). The rate of CO_2 production at 275°C was independent of the time of irradiation throughout the whole $[O_2]/[CO]$ range covered, indicating that at this temperature the equilibrium concentration of O_3 is too small for HgO formation to occur. The $[O_2]/[CO]$ ratio was changed from 0.00273 to 450, greater than five orders of magnitude. At any given total pressure (experiments were done at ~ 50, 100, and 500 torr) $\Phi\{CO_2\}$ rises to a maximum as the ratio of $[O_2]$ to $[CO]$ increases and then declines on further increase in $[O_2]/[CO]$. For $[O_2]/[CO]$ below 0.08, a change in the total pressure from ~ 50 - 500 torr has no effect on $\Phi\{CO_2\}$, but for $[O_2]/[CO]$ above 0.08, $\Phi\{CO_2\}$ increases with increasing total pressure. Some runs were done where the major gas was CF_4, and some where it was N_2 (Table IV). The presence of excess CF_4 in the pressure independent regions had no effect upon $\Phi\{CO_2\}$. In the pressure dependent region increasing the total pressure with CF_4 has the same effect as increasing both the $[O_2]$ and $[CO]$, while keeping $[O_2]/[CO]$ constant. The presence of excess N_2 in the pressure-independent region had no effect upon $\Phi\{CO_2\}$, but in the pressure dependent region $\Phi\{CO_2\}$ is not enhanced nearly as much

TABLE II

The Hg-Sensitized Oxidation of CO at 275°C[a]

$[O_2]$, torr	[CO], torr	$[O_2]/[CO]$	Irradiation time, min.	$\Phi\{CO_2\}$
Total Pressure ~ 500 torr				
498	1.10	453	10.0	0.0897
535	3.60	149	32.0	0.147
684	6.5	105	30.0	0.189
494	5.20	95.0	20.0	0.171
483	14.5	33.3	10.5	0.182
471	26.0	18.1	10.0	0.240
437	70.0	6.25	10.0	0.295
396	101	3.93	10.0	0.322
430	190	2.26	10.0	0.343
282	220	1.28	10.0	0.397
218	289	0.754	10.0	0.432
207	290	0.715	10.0	0.424
138	360	0.383	10.0	0.452
80	425	0.188	11.0	0.435
61	441	0.138	10.0	0.423
5.50	501	0.0101	10.0	0.150
5.00	491	0.0102	25.0	0.131
3.80	501	0.00780	17.0	0.107
2.25	496	0.00453	35.0	0.0720
1.35	497	0.00272	30.0	0.0500
Total Pressure ~ 100 torr				
96	22	4.36	15.0	0.200
97	23	4.22	10.0	0.245
67	30	2.23	35.0	0.293
67	30	2.23	4.00	0.276
117	64	1.83	30.0	0.143
49	60	0.818	10.0	0.364
38	68	0.599	5.00	0.372
50	125	0.400	5.00	0.397*
24	88	0.272	81.0	0.416
18	89	0.203	10.0	0.397
9.90	104	0.0950	6.00	0.360
6.70	94.0	0.0715	10.0	0.359
5.4	103	0.0525	5.00	0.274*
4.70	99	0.0475	95.0	0.325
4.10	109	0.0376	10.0	0.295
2.65	105	0.0252	10.0	0.244
2.70	109	0.0247	30.0	0.234
1.50	99	0.0152	10.0	0.177
1.10	111	0.0099	10.0	0.135

TABLE II (Cont.)

$[O_2]$, torr	[CO], torr	$[O_2]/[CO]$	Irradiation time, min.	$\Phi\{CO_2\}$
Total Pressure ~ 50 torr				
26.0	9.75	2.66	10.0	0.212
32.5	17.5	1.85	10.0	0.247
20	30	0.668	10.0	0.330
20	32	0.628	10.0	0.328
12	38	0.316	10.0	0.363
5.70	44	0.130	15.0	0.352
1.90	48	0.0396	25.0	0.246
1.05	49	0.0214	15.0	0.192

[a] $I_a = 4.57 \times 10^{-9}\ \frac{\text{Einsteins}}{\text{cc - min}}$ in all runs except those marked with an asterisk, when $I_a = 0.252 \times 10^{-9}\ \frac{\text{Einsteins}}{\text{cc - sec}}$.

TABLE III

The Hg-Sensitized Oxidation of CO in the Presence of 2-Trifluoromethylpropene at 275°C[a]

$[O_2]$, torr	[CO], torr	$[O_2]$/[CO]	[TMP], torr	Irradiation time, min.	$\Phi\{CO_2\}$	$\Phi\{E\}$	$\Phi\{A\}$	$\Phi\{E\}+\Phi\{A\}$	$\Phi\{E\}/\Phi\{A\}$
				High $[O_2]/[CO]$ Regime					
331	177	1.87	3.70	5.75	0.164	0.210	0.135	0.35	1.56
300	188	1.60	22.0	6.00	0.114	0.202	0.118	0.33	1.71
214	287	0.745	3.80	6.00	0.208	0.186	0.118	0.30	1.57
210	357	0.589	1.15	6.00	0.267	0.174	0.102	0.28	1.71
190	322	0.590	4.00	6.00	0.240	0.195	0.128	0.32	1.52
198	363	0.545	22.0	6.00	0.145	0.200	0.125	0.33	1.60
176	324	0.543	3.60	6.00	0.215	-	-	-	-
171	328	0.521	1.30	6.00	0.214	0.171	0.102	0.27	1.68
91	394	0.231	10.0	6.00	0.216	0.190	0.114	0.30	1.66
96	420	0.229	1.10	6.00	0.268	0.152	0.094	0.24	1.62
95	395	0.240	22.0	6.00	0.173	0.166	0.090	0.26	1.84
92	414	0.222	1.20	6.00	0.274	0.154	0.0813	0.25	1.90
				Low $[O_2]/[CO]$ Regime					
82	432	0.190	3.90	6.00	0.240	0.183	0.113	0.30	1.62
23	475	0.0485	3.55	5.00	0.167	0.109	0.069	0.28	1.58
11.5	483	0.0238	4.00	4.00	0.130	0.0752	0.052	0.13	1.73
1.40	81.0	0.0173	0.995	10.0	0.132	-	-	-	-
1.40	78.0	0.0179	0.400	10.0	0.160	0.060	0.0367	0.097	1.63
12.0	490	0.0245	3.50	16.0	0.130	0.076	0.047	0.12	1.61
1.14	80	0.0143	0.560	10.0	0.130	-	-	-	-
3.65	496	0.00735	0.590	15.0	-	0.0303	0.0162	0.047	1.87
3.60	493	0.00730	3.60	15.0	0.0690	0.0336	0.011	0.045	3.05
3.70	516	0.00717	0.700	15.0	0.081	-	-	-	-
2.57	500	0.00533	0.730	10.0	0.065	-	-	-	-
2.20	503	0.00437	3.45	15.0	0.415	0.0255	0.0144	0.040	1.77
2.00	523	0.00382	0.530	15.0	0.407	0.0144	0.0067	0.021	2.15
1.60	503	0.00138	3.10	31.0	0.034	0.0169	0.0057	0.023	2.96

[a] $I_a = 4.57 \times 10^{-9}\ \frac{\text{Einsteins}}{\text{cc - min.}}$.

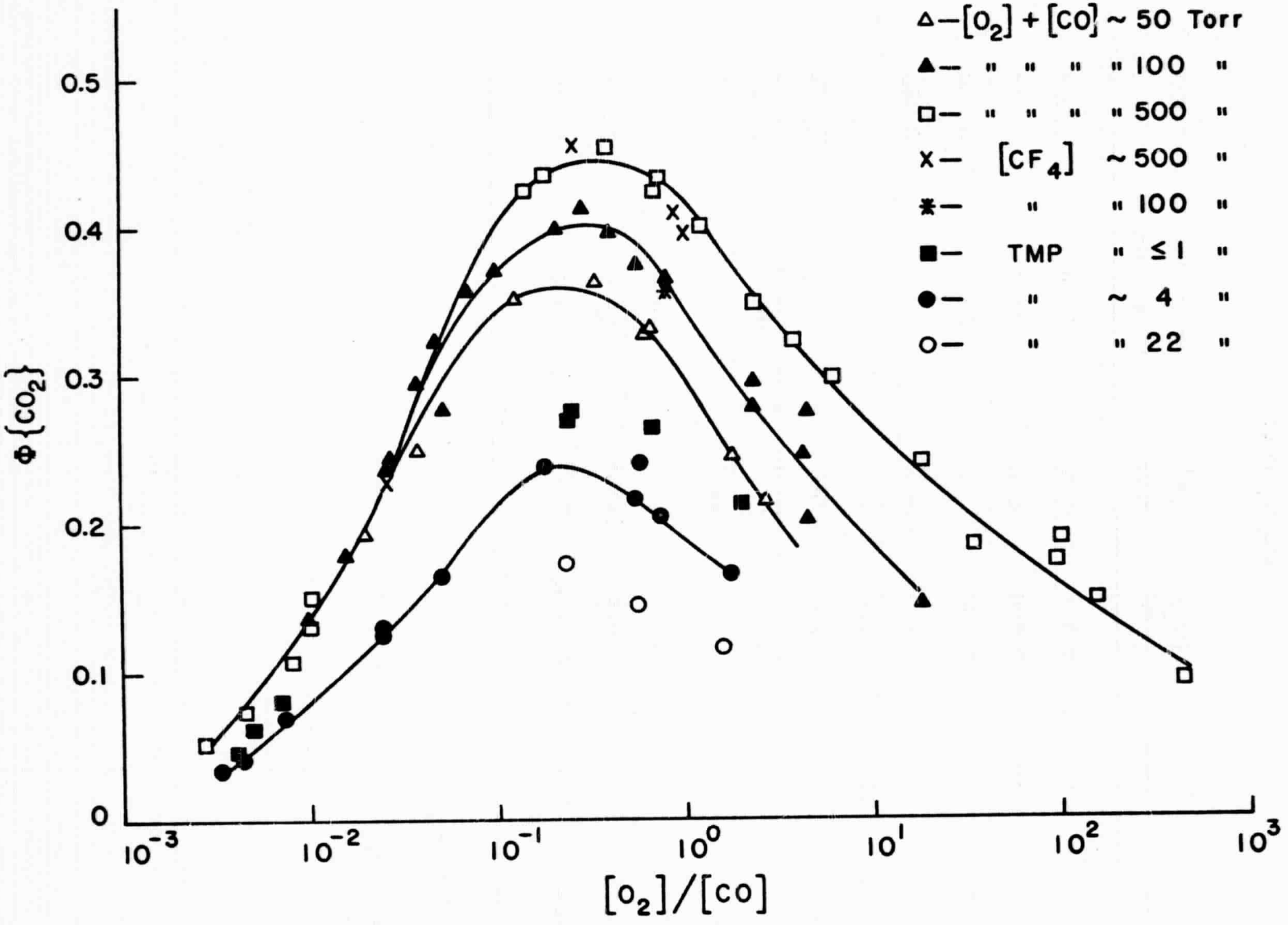


Figure 1

Plots of $\Phi\{CO_2\}$ vs. $[O_2]/[CO]$ in the absence and in the presence of TMP at 275°C.

TABLE IV

The Hg-Sensitized Oxidation of CO in the Presence of CF_4 and N_2 at 275° C

$[O_2]$, torr	[CO], torr	$[O_2]$/[CO]	[X], torr	Irradiation time, min.	$\Phi\{CO_2\}$
50	53	0.945	418[a]	20.0	0.392
27	30	0.900	441[a]	22.0	0.410
24.5	31	0.790	96[a]	20.0	0.354
11	41.5	0.265	482[a]	21.0	0.455
2.60	100	0.026	411[a]	20.25	0.226
68	34	2.00	600[b]	20.0	0.320
65	36	1.80	614[b]	10.0	0.324
33	18.5	1.78	663[b]	20.0	0.290
20	31	0.646	664[b]	20.0	0.310
2.75	97	0.0284	550[b]	25.0	0.236
3.15	114	0.0276	523[b]	30.0	0.220

[a] $X = CF_4$

[b] $X = N_2$

as when the other gases were used to raise the pressure. In two runs the intensity, I_a, was changed by a factor of 18 with no effect upon $\Phi\{CO_2\}$.

In the presence of TMP for $[O_2]/[CO] < 0.08$, $\Phi\{CO_2\}$ is reduced by about a factor of 2 and $\Phi\{CO_2\}$ is close to $\Phi\{E\} + \Phi\{A\}$ providing $[CO]/[TMP] < 200$. For $[CO]/[TMP] > 200$, $\Phi\{CO_2\} > \Phi\{E\} + \Phi\{A\}$. The average value for $\Phi\{E\}/\Phi\{A\} = 1.63$ for the runs of ≤ 10 minutes duration. Within experimental errors this value is the same as that obtained for the reaction of O atoms with TMP at 275°C. A complication observed at 275°C is a thermal decomposition of the aldehyde to give some CO_2. The last run in Table V illustrates this. In this run the contents of the cell were allowed to remain in the cell for 120 minutes after irradiation. $\Phi\{CO_2\}$ increased by about a factor of 2, whereas the aldehyde yield was reduced by 90%. In most runs the contribution to $\Phi\{CO_2\}$ due to the dark reaction is small, but it does account for the smaller yield of the aldehyde for longer duration runs.

In the presence of TMP for $[O_2]/[CO] > 0.08$, $\Phi\{CO_2\}$ is also about a factor of 2 less than in the absence of TMP. $\Phi\{CO_2\} \approx \Phi\{A\} + \Phi\{E\}$ if $[CO]/[TMP] \geq 350$ and $\Phi\{CO_2\} < \Phi\{E\} + \Phi\{A\}$ for $[CO]/[TMP] < 350$.

The results for runs in the absence of CO at 275°C are presented in Table V. Except for the run in which the products were kept in the cell after irradiation there is no effect on $\Phi\{CO_2\}$, $\Phi\{E\}$, or $\Phi\{A\}$ when $[O_2]/[TMP]$ was changed from 22 - 240. $\Phi\{E\} + \Phi\{A\}$ exceeds $\Phi\{CO_2\}$ by about a factor of 10 and the average $\Phi\{E\}/\Phi\{A\} = 1.56$. The value of 1.56 for $\Phi\{E\}/\Phi\{A\}$ at 275°C is the same as in the presence of CO, unlike at 25°C, and the same as for the reaction of O atoms with TMP.

TABLE V

The Hg-Sensitized Oxidation of 2-Trifluoromethylpropene at 275°C[a]

$[O_2]$, torr	[TMP], torr	Irradiation time, min.	$\Phi\{CO_2\}$	$\Phi\{E\}$	$\Phi\{A\}$	$\Phi\{E\} + \Phi\{A\}$	$\Phi\{E\}/\Phi\{A\}$
667	3.20	6.00	0.055	0.175	0.122	0.30	1.43
343	4.50	6.00	-	0.178	0.121	0.30	1.47
192	3.50	6.00	-	0.152	0.0985	0.25	1.54
328	1.60	6.00	0.055	0.151	-	-	-
118	3.70	6.00	0.053	0.159	0.092	0.25	1.72
285	5.25	6.00	0.046	0.166	0.103	0.27	1.60
266	1.10	6.00	0.048	0.157	0.099	0.27	1.59
273[b]	1.50	6.00	0.117	0.157	0.0135	0.17	11.6

[a] $I_a = 4.57 \times 10^{-9} \dfrac{\text{Einsteins}}{\text{cc - min.}}$

[b] After irradiation the cell contents remained in the cell for 120 minutes at 275° C.

TABLE VI

Relative Rate Constants for the Hg-Sensitized Oxidation of CO

Rate Constant Ratio	Value	Temperature °C	Source
k_b/k_a	1.08	275	Eqn. I, Fig. 2
	1.23	25	Eqn. I, Fig. 2
k_7/k_6	2.4	275	Eqn. VIII, Fig. 3 - no TMP
	2.2	275	Eqn. IX, Fig. 3 - TMP
	2.2	275	Eqn. X, Fig. 4
	~ 3	25	Eqn. IX, Fig. 5
k_8/k_6	0.104	275	Eqn. VIII, Fig. 3 - no TMP
	0.085	275	Eqn. IX, Fig. 3 - TMP
	0.104	275	Eqn. X, Fig. 4
	0.24	25	Eqn. IX, Fig. 5
$(k_{13}+k_{14})/(k_9+k_{12})$	0.20	275	Eqn. XI, Fig. 6
k_{14}/k_{13}	12.0	275	Eqn. XI, Fig. 6
k_{12}/k_9	3.25	275	Eqn. XII, Fig. 7
k_{11}/k_{10}	25 torr	275	Eqn. XII, Fig. 7
k_{13}/k_9	0.067	275	
k_{14}/k_9	0.81	275	
k_{12}/k_{13}	55	275	
$(k_9+k_{12})/k_{21}$	0.06	275	Eqn. XIII, Table III
$(k_{13}+k_{14})/k_{21}$	0.012	275	

In order to be able to adjust [TMP] to prevent the quenching of $Hg(^3P_1)$ by TMP, it was necessary to know the quenching coefficient for $Hg(^3P_1)$ by TMP. This was determined at 25°C and 275°C by following the effect of [TMP] on N_2 formation in the mercury sensitized decomposition of N_2O-TMP mixtures. The reaction scheme is

$$Hg(^1S_o) + h\nu \rightarrow Hg(^3P_1)$$

$$Hg(^3P_1) + N_2O \rightarrow N_2 + O + Hg(^1S_o) \qquad \text{(a)}$$

$$Hg(^3P_1) + TMP \rightarrow Hg(^1S_o) + TMP \qquad \text{(b)}$$

This scheme leads to

$$\Phi\{N_2\}^{-1} = 1 + \frac{k_b\,[TMP]}{k_a\,[N_2O]} \qquad \text{I}$$

The data is presented in Figure 2 as a plot of $\Phi\{N_2\}^{-1}$ vs. [TMP]/[N_2O]. From the slopes $k_b/k_a = 1.23$ at 25°C and $k_b/k_a = 1.08$ at 275°C, though these values are the same within the experimental uncertainty. For all the experiments with TMP added to the O_2 or CO - O_2 mixtures, [TMP] was kept sufficiently small so that reaction b was negligible.

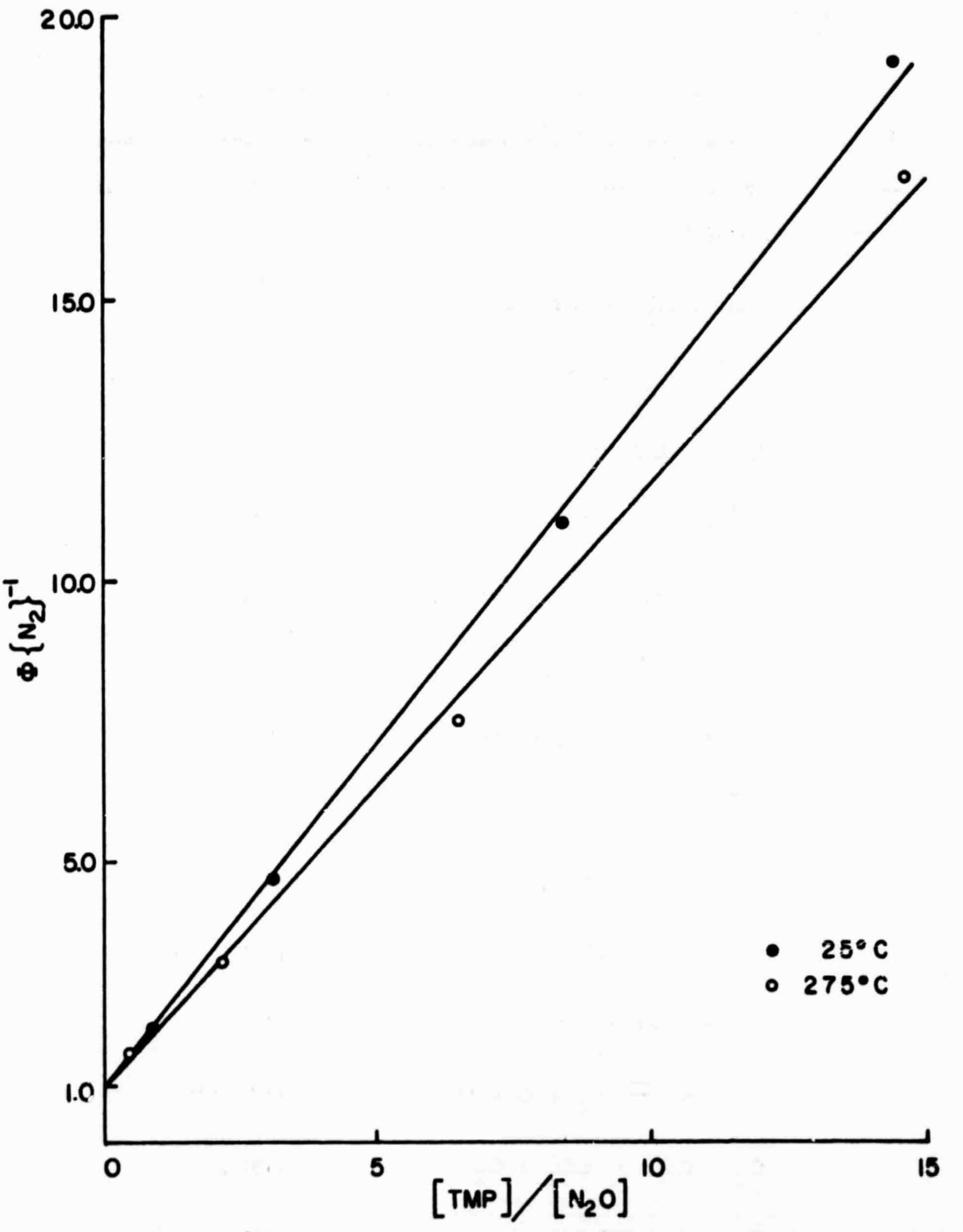


Figure 2

Plots of $\Phi\{N_2\}^{-1}$ vs. [TMP]/[N_2O] in the Hg-sensitized decomposition

DISCUSSION

The initial steps in the Hg-sensitized oxidation of CO will be all the reactions deactivating $Hg(^3P_1)$ and $Hg(^3P_o)$, reactions 1-5. The subsequent reactions proposed to account for the results at 275°C and in the absence of TMP are the following:

$$CO^{\dagger} + O_2 \rightarrow CO_2 + O \quad (6)$$

$$CO^{\dagger} + O_2 \rightarrow CO + O_2 \quad (7)$$

$$CO^{\dagger} + CO \rightarrow 2\,CO \quad (8)$$

$$O_2^* + CO \rightarrow CO_3 \quad (9)$$

$$CO_3 + M \rightarrow CO_2 + O + M \quad (10)$$

$$CO_3 \rightarrow CO + O_2 \quad (11)$$

$$O_2^* + CO \rightarrow O_2 + CO \quad (12)$$

$$O_2^* + O_2 \rightarrow O_3 + O \quad (13)$$

$$O_2^* + O_2 \rightarrow 2\,O_2 \quad (14)$$

$$O + CO \rightarrow CO_2 \quad (15)$$

$$O \rightarrow \text{Wall removal} \quad (16)$$

$$O_3 + M \rightleftarrows O_2 + O + M \quad (17, -17)$$

$$O_3 + CO \rightarrow CO_2 + O_2 \quad (18)$$

$$O_3 + O \rightarrow 2\,O_2 \quad (19)$$

The asterisk indicates electronically excited O_2 and the dagger indicates vibrationally excited CO having sufficient energy to be able to undergo reaction 6. The O_2^* produced in reactions 1 and 2 may not be the same, but the concentration of the state produced in the latter reaction will usually be unimportant compared to that produced in reaction 1. From the scheme comprising reactions 1-5, the fraction of O_2^* produced by reaction 1 is given by

$$\frac{R\{1\}}{R\{1\} + R\{2\}} = \frac{1 + k_4[CO]/k_2[O_2]}{1 + (k_4/k_2 + k_5/k_1)\,[CO]/[O_2]}$$

The ratios $k_1/(k_3 + k_5)$ and k_4/k_2 are 3.41 and 0.40, respectively.[12] Since $k_5/(k_3 + k_5)$ is 0.78,[6] it can be computed that the minimum value of $R\{1\}/(R\{1\} + R\{2\})$, i.e. when $[O_2]/[CO] \rightarrow 0$, is 0.64. Under conditions where the reactions of O_2^* become important, i.e. $[O_2]/[CO] \sim 0.2$ (see below), $R\{1\}/(R\{1\} + R\{2\})$ will be 0.72 and will increase as $[O_2]/[CO]$ increases.

Reaction 6 is postulated here for the first time. Reaction 8 is simply a collisional deactivation of the excited CO, but reaction 7 is probably a sum of collisional deactivation and deactivation via the same intermediate or transition state as in reaction 6. Reaction 9 has not been previously postulated, but the quenching of O_2^* by CO has been studied.[2] Presumably the intermediate to product formation is assymmetric CO_3. This species may be different than the symmetric CO_3 which is formed in the $O(^1D) + CO_2$ system at high pressures[8] and whose low temperature infrared spectrum has been obtained.[13, 14] Reaction 10 is a pressure induced dissociation of CO_3. The pressure dependence is needed to account for the pressure effect shown in Figure 1. Reactions 11 and 12 comprise the deactivation of O_2^* by CO through the CO_3

intermediate and by collisional quenching, respectively. Reactions 13 and 14, together with their relative importance, have been previously observed.[1] The O_3 formed in reaction 13 will be unstable at 275°C and will readily decompose according to reaction 17, or it may also react with CO to give CO_2, reaction 18. Reaction 18 has been proposed from time to time, though the evidence indicates that this reaction is unimportant even at 275°C.[15] At higher $[CO]/[O_2]$ the oxygen atoms will react with CO to give CO_2, but as the $[CO]/[O_2]$ decreases the O atoms must eventually be lost by either reaction 16 or 19 or both. Reaction 16 has been shown to occur in a quartz reaction vessel.[16] Reaction 19 is well known at room temperature and will certainly occur at higher temperatures if the $[O_3]$ is sufficiently high for its rate to compete with the rate of reaction 16.

Reactions 6-19 are the most reasonable reactions consistent with the experimental data. Other reasonable reactions will be discussed later and demonstrated to be unimportant.

In the presence of TMP the additional reactions that need to be considered are

$$O + TMP \rightarrow \alpha E + (1 - \alpha) A \qquad (20)$$

$$O_2^* + TMP \rightarrow a\,CO_2 + bE + cA \qquad (21)$$

where α is the fraction of oxygen atoms that give E (i.e. $\alpha = 0.60$), and a, b, c are undetermined coefficients. Only a limited range of experimental conditions was accessible at room temperature, so that only the partial mechanism consisting of reactions 1-8, 20 and 21 need be considered.

The reaction of O_2^* with some perfluorinated olefins has been studied, and it has been concluded that the reaction proceeds via excited olefin[3]

$$O_2^* + \text{Olefin} \rightarrow O_2 + (\text{Olefin})^*$$

$$O_2 + (\text{Olefin})^* \rightarrow \text{Products.}$$

This may also be the case for TMP, but our data is insufficient to show this. The formation of the aldehyde and epoxide in the absence of CO at 275°C in the same ratio as is obtained in the reaction of oxygen atoms with TMP (Table V) would suggest that oxygen atoms are also involved in the O_2-TMP system. Atoms could be formed either via reaction 13 or 22

$$O_2^* + M \rightarrow 2O + M \qquad (22)$$

The fact that $\Phi\{E\}$ and $\Phi\{A\}$ are independent of $[O_2]/[TMP]$ and the fact that > 80% of all O_2^* react with TMP $[(k_{13} + k_{14})/k_{21} \sim 0.01$ as determined later$]$ argues against the formation of these products from oxygen atoms produced in reaction 13. Reaction 22 cannot be important either, because $\Phi\{E\}$ and $\Phi\{A\}$ are independent of $[O_2]/[TMP]$, and $\Phi\{E\} + \Phi\{A\} << 2$. An alternative explanation is that reactions 20 and 21 at 275°C proceed via a common biradical intermediate such as suggested for the reaction of oxygen atoms with TMP,[9] the reaction scheme being the following:

$$O_2 + \text{Olefin} \rightarrow \cdot C{-}C{-}O{-}O\cdot$$

$$\cdot C{-}C{-}O{-}O\cdot + \text{Olefin} \rightarrow \cdot C{-}C{-}O{-}O{-}C{-}C\cdot \xrightarrow{25^\circ C} aCO_2 + bE + cA$$

$$\xrightarrow{275^\circ C}$$

$$O + \text{Olefin} \rightarrow \cdot C{-}C{-}O\cdot \rightarrow \alpha E + (1 - \alpha) A$$

At the elevated temperature the O - O bond rupture of the peroxide intermediate occurs prior to reaction and the products are the same as from the O atom addition. At room temperature incipient product formation from the peroxide intermediate occurs prior to complete O - O bond rupture because of the smaller energy, and $\Phi\{E\}/\Phi\{A\}$ is not the same as for O-atom addition.

The application of the steady-state hypothesis to the mechanism consisting of reactions 1-19 leads to the following expression for $\Phi\{CO_2\}$ in the absence of TMP

$$\Phi\{CO_2\} + (R\{16\} + 2R\{19\})/I_a = f'\Phi' + f''\Phi'' \qquad \text{II}$$

where R{16} and R{19} are the rates of reactions 16 and 19, respectively, f' is the fraction of the radiation which produces $CO^{\dagger}$, f'' is the fraction of the radiation that produces O_2^* (note that $f' + f'' = 1$), Φ' is the fraction of the $CO^{\dagger}$ produced that yields products, and Φ'' is the fraction of the O_2^* produced that yields products. The specific expressions for the four terms on the right-hand side of Equation II are

$$f' = \frac{[CO]\{k_3 + k_4k_5[CO]/(k_2[O_2] + k_4[CO])\}}{k_1[O_2] + (k_3 + k_5)[CO]} \qquad \text{III}$$

$$f'' = \frac{[O_2]\{k_1 + k_2k_5[CO]/(k_2[O_2] + k_4[CO])\}}{k_1[O_2] + (k_3 + k_5)[CO]} \qquad \text{IV}$$

$$\Phi' = 2k_6[O_2]/\{(k_6 + k_7)[O_2] + k_8[CO]\} \qquad \text{V}$$

$$\Phi'' = \frac{2\beta k_9[CO] + 2k_{13}[O_2]}{(k_9 + k_{12})[CO] + (k_{13} + k_{14})[O_2]} \qquad \text{VI}$$

where $\beta \equiv k_{10}[M]/(k_{10}[M]+k_{11})$. VII

Equation II is a complex function of the reactant pressures, but depends primarily on the $[O_2]/[CO]$ ratio. For the evaluation of rate constants, it is convenient to divide the range of $[O_2]/[CO]$ ratios into a high $[O_2]/[CO]$ regime and a low $[O_2]/[CO]$ regime.

Low $[O_2]/[CO]$ Regime

We assume that steps 9-14, 16 and 19 are unimportant at low $[O_2]/[CO]$. Under these conditions, expression II reduces to

$$f'\Phi\{CO_2\}^{-1} = (\Phi')^{-1} = \frac{1}{2}\left(1+\frac{k_7}{k_6}+\frac{k_8}{k_6}\frac{[CO]}{[O_2]}\right) \qquad \text{VIII}$$

A plot of the left-hand side of Equation VIII vs. $[CO]/[O_2]$ should be linear with the intercept equal to $(1/2)(1+k_7/k_6)$ and the slope equal to $k_8/2k_6$. Values of f' were calculated from the known quenching rate constants of $Hg(^3P_1)$ and $Hg(^3P_o)$ by CO and O_2. These values are: $k_1/(k_3+k_5) = 3.41$,[12] $k_4/k_2 = 0.40$,[12] and $k_5/(k_3+k_5) = 0.78$.[6] Figure 3 presents the plot of the experimental data in accordance with expression VIII. The plot is linear for $[CO]/[O_2] > 20$, but as $[CO]/[O_2]$ drops below 20 the slope changes sharply. Thus, the assumption that reactions 9-14, 16 and 19 are negligible breaks down at $[CO]/[O_2] = 20$. The slope of the linear portion of the line gives $k_8/k_6 = 0.104$ and the intercept gives $k_7/k_6 = 2.4$.

The experiments in the presence of TMP at low $[O_2]/[CO]$ ratios demonstrate the formation of oxygen atoms. First of all, both the epoxide and aldehyde are formed in the same ratio as in the O - TMP system. This in itself is not sufficient evidence, since reaction 21 also gives the same products in the same ratio. However, the quantum

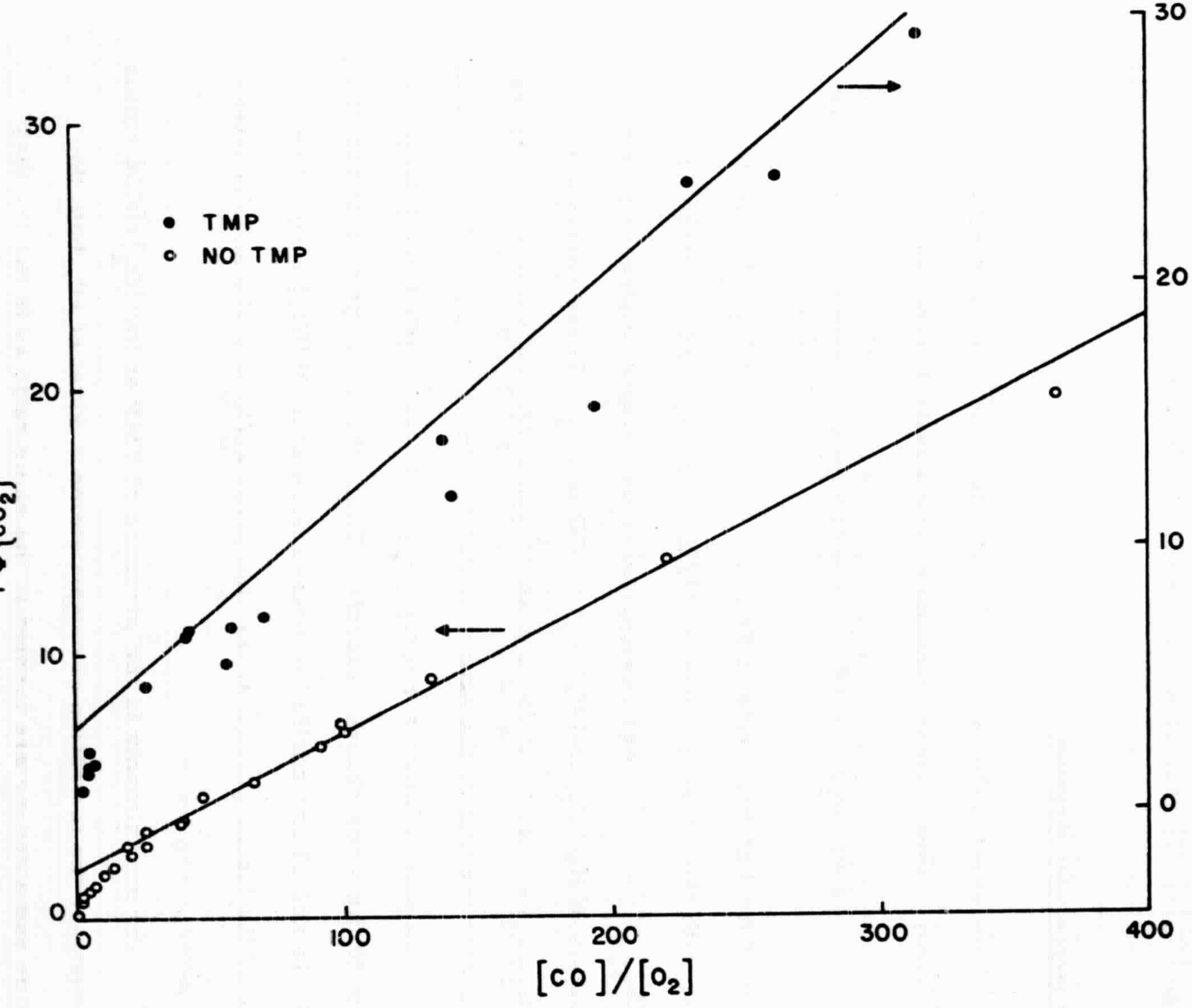


Figure 3

Plot of $f'\Phi\{CO_2\}^{-1}$ vs. $[CO]/[O_2]$ in the presence and in the absence of TMP at 275°C.

yields are at least a factor of 10 too large to be explained by reaction 21. Secondly $\Phi\{CO_2\}$ depends on the [CO]/[TMP] ratio as predicted from the known relative constants for the reaction of O atoms with CO and TMP.[10]

The mechanism predicts that in the presence of TMP under conditions where all the oxygen atoms are scavenged that $\Phi\{CO_2\}$ be reduced by a factor of 2 and that $\Phi\{CO_2\} = \Phi\{E\} + \Phi\{A\}$. Examination of Figure 1 shows that for high $[CO]/[O_2]$ ratios and for [CO]/[TMP] < 150, $\Phi\{CO_2\}$ is reduced by about a factor of 2 and examination of Table III shows that for high $[CO]/[O_2]$ and for [CO]/[TMP] < 150, $\Phi\{CO_2\} \approx \Phi\{E\} + \Phi\{A\}$. The expression which applies in the presence of TMP is

$$f'\Phi\{CO_2\}^{-1} = 1 + k_7/k_6 + k_8[CO]/k_6[O_2] \qquad \text{IX}$$

A plot of $f'\Phi\{CO_2\}$ vs. $[CO]/[O_2]$ should be linear with a slope of k_8/k_6 and an intercept of $1 + k_7/k_6$. This plot also is shown in Figure 3. The plot is reasonably linear for $[CO]/[O_2] > 20$, but the slope changes as $[CO]/[O_2]$ drops below 20, because the reactions of O_2^* with CO and O_2 become important. The points for $[CO]/[O_2] < 20$ and for larger [CO]/[TMP] ratios (runs with ~ 1 torr TMP, Table III) lie lower than those at lower [CO]/[TMP] ratios (runs with 4-22 torr TMP). The reason for this being that at lower [CO]/[TMP] reaction 21 becomes important. In the linear portion the points for which [CO]/[TMP] > 500 lie below the line, because not all the O atoms are scavenged by TMP, as a calculation using the known relative rate constants[10] for reactions 15 and 20 indicates. The slope and intercept give, respectively, $k_8/k_6 = 0.085$ and $k_7/k_6 = 2.2$.

Since $\Phi\{CO_2\} = \Phi\{E\} + \Phi\{A\}$ and since $\Phi\{E\}/\Phi\{A\} = 1.5$, a plot of either $f'(\Phi\{E\} + \Phi\{A\})^{-1}$ or $f'\Phi\{E\}^{-1}$ vs. $[CO]/[O_2]$ also should be linear for $[CO]/[O_2] \geq 20$. Figure 4 is a plot of $f'\Phi\{E\}^{-1}$ vs. $[CO]/[O_2]$, and it should fit the expression

$$f'\Phi\{E\}^{-1} = 1.67(1 + k_7/k_6) + 1.67 k_8[CO]/k_6[O_2] \qquad \text{X}$$

A plot involving $\Phi\{E\} + \Phi\{A\}$ is not shown because some of the aldehyde decomposed, thus making the measured values of $\Phi\{A\}$ somewhat lower than they should be. The slopes and intercept of Figure 4 give, respectively, $k_8/k_6 = 0.104$ and $k_7/k_6 = 2.2$.

The addition of excess N_2 or CF_4 in the low $[O_2]/[CO]$ regime has no effect upon $\Phi\{CO_2\}$. Both N_2 and CF_4 are very poor quenchers of $Hg(^3P)$,[12, 17] but it is somewhat surprising that they are also such poor quenchers of $CO^\dagger$. Thus our results show that O_2 is much more effective than CO, which in turn is much more effective than N_2 and CF_4 in removing $CO^\dagger$. Foster and Kimbell[18] have shown that N_2 can remove low vibrational levels of CO, but it is relatively inefficient in depopulating levels for $v \sim 9$. Consequently $CO^\dagger$ must represent the higher vibrational levels ($v \sim 9$) of CO.

At room temperature the upper value for $[O_2]/[CO]$ was limited to 0.19, because of the requirements that $[O_2]/[TMP] < 5$ and $([O_2] + 0.29[CO])/[TMP] > 10$. The mechanism predicts that if oxygen atoms are produced in reaction 6 then $\Phi\{E\}/\Phi\{A\} = 1.50$ and, if complete scavenging occurs, $\Phi\{CO_2\} = \Phi\{E\} + \Phi\{A\}$. The data in Table I show that this is approximately the case for the second condition and that the average value of $\Phi\{E\}/\Phi\{A\} = 1.50$. The small difference between $\Phi\{CO_2\}$ and $\Phi\{E\} + \Phi\{A\}$ in some of the runs can be explained by

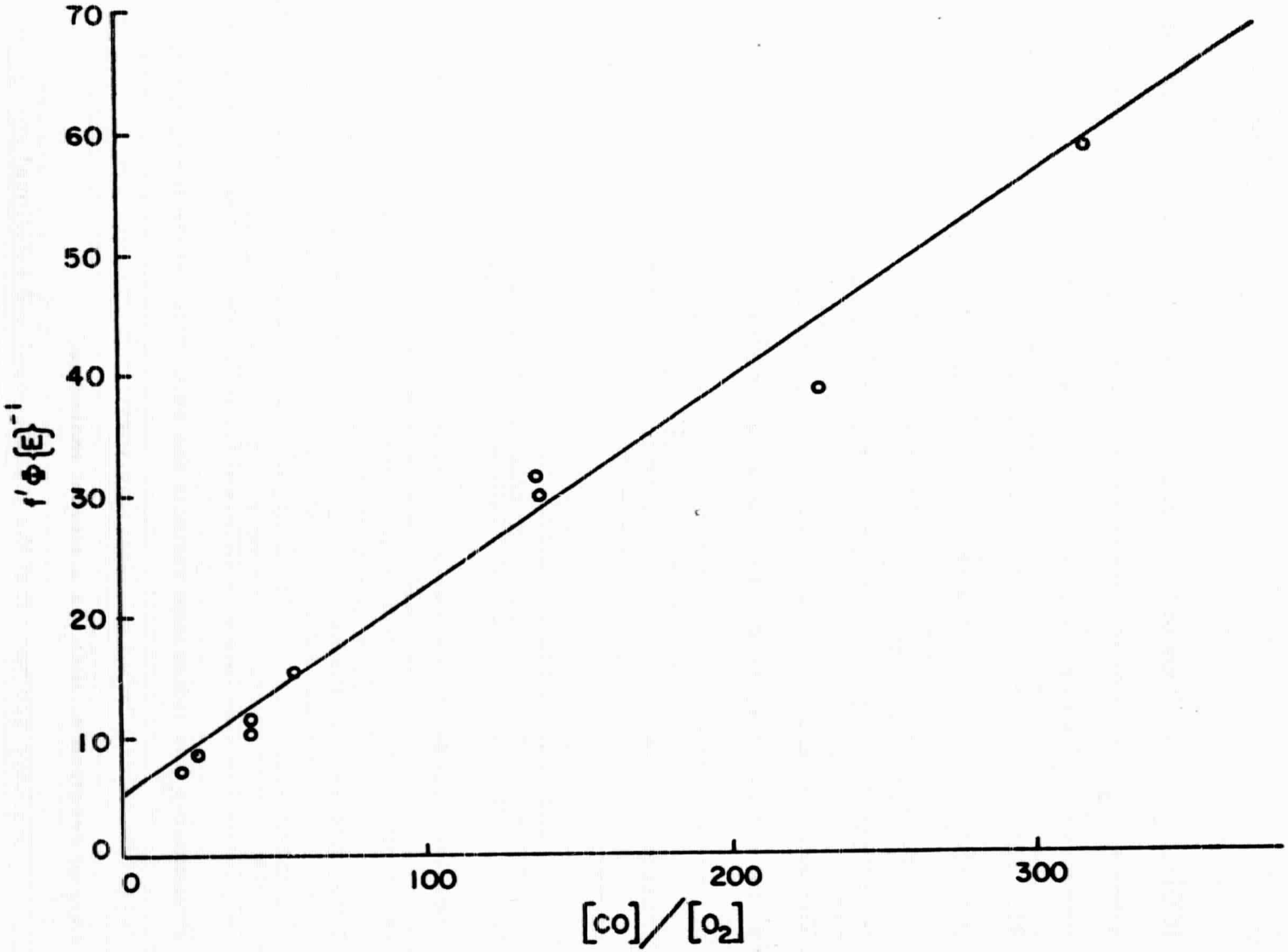


Figure 4

Plot of $f'\Phi\{E\}^{-1}$ vs. $[CO]/[O_2]$ at 275°C.

incomplete scavenging of the oxygen atoms, the extent of scavenging being just about what is expected from the known value for k_{20}/k_{15} at room temperature.[10] Figure 5 presents a plot of $f'\Phi\{CO_2\}^{-1}$ vs. $[CO]/[O_2]$. The slope of this plot gives $k_8/k_6 = 0.24$ and the intercept gives $k_7/k_6 \sim 3$. For the run at the lowest $[CO]/[O_2]$ a small correction to $\Phi\{CO_2\}$ was made to account for the contribution from reaction 21. The line in Figure 5 indicates no curvature even at the lowest $[CO]/[O_2]$, contrary to the results at 275°C. This is reasonable because $(k_{14} + k_{13})/k_{21}$ will be shown to be 0.012 at 275°C, and since $[O_2]/[TMP] \lesssim 5.0$, more than 90% of the O_2^* will be scavenged by TMP. The points with 19.4, 21.2, and 24 torr O_2, the dark points in Figure 5, lie somewhat above the line, because for these runs $[O_2]/[TMP] \geq 5$, and the time of irradiation for two of these runs was relatively long; consequently some O_3, and therefore some HgO, formation may have occurred.

The observed temperature effect on k_8/k_6, but not on k_7/k_6, indicates that reactions 6 and 7 have equal and probably small activation energies. An activation energy for reaction 8 is not expected since it is simply a collisional deactivation of $CO^\dagger$. On the other hand reaction 7 may proceed via the same complex or transition state as reaction 6. The independence of reaction 6 on [M] clearly shows that the intermediate CO_3 formed in reaction 6 is different from the one formed in reaction 9. Presumably this difference reflects the spin state, since the spin conservation rules predict a triplet intermediate in reaction 6 but a singlet CO_3 in reaction 9, if O_2^* is a singlet molecule.

We have assumed that the translational and rotational energy of the initially produced CO in reactions 3 and 4 is rapidly lost and that the

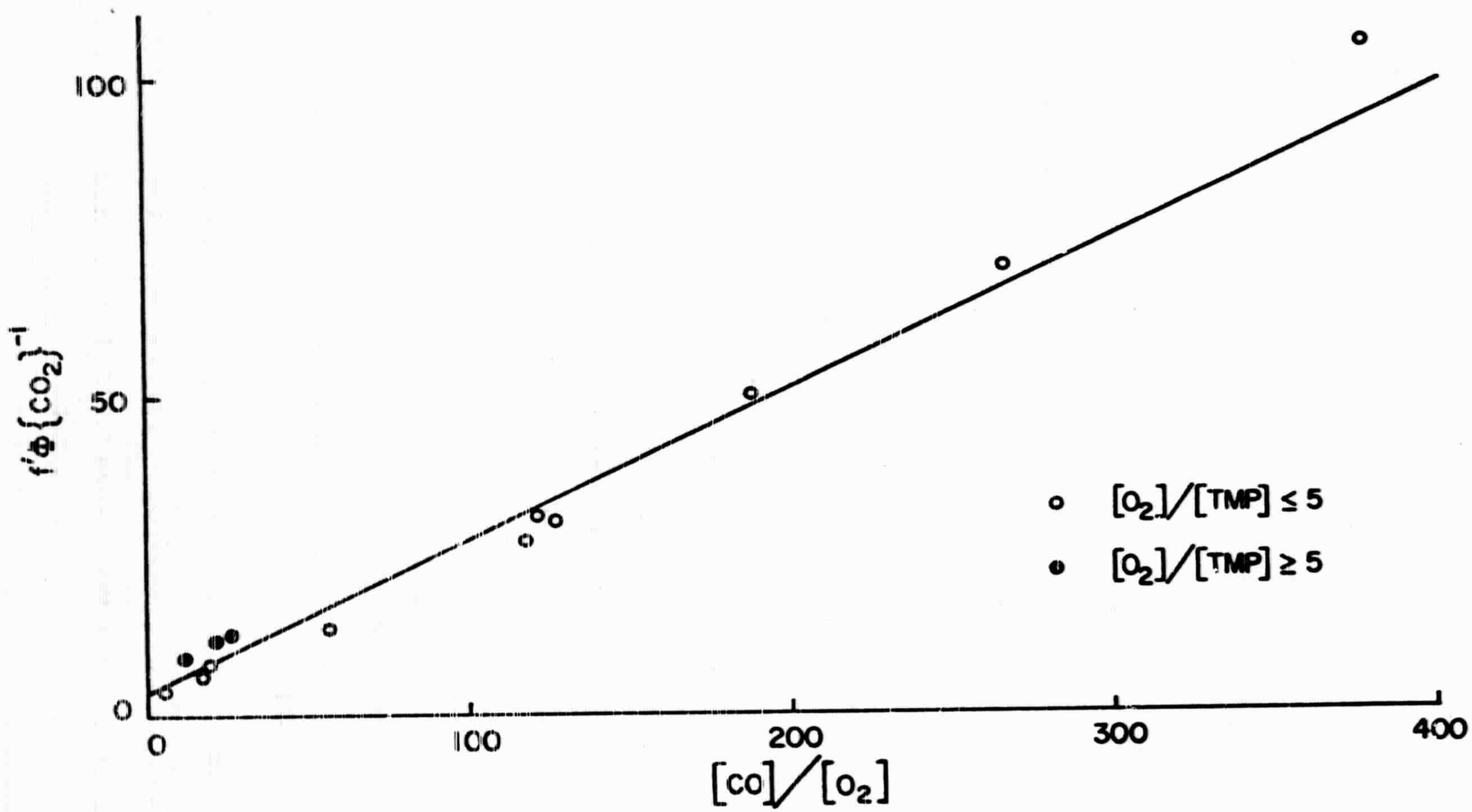


Figure 5

Plot of $f'\Phi\{CO_2\}^{-1}$ vs. $[CO]/[O_2]$ at 25°C. The value of the point at the lowest $[CO]/[O_2]$ ratio was corrected for the contribution of reaction 21 to $\Phi\{CO_2\}$.

reactive species in reactions 6-8 is vibrationally excited CO. The results support this assumption, since the value for $(k_6 + k_7)/k_8 = 13$-50 is much too large to be consistent with reaction 8 being translational or rotational energy quenching. Further support comes from the fact that both N_2 and CF_4 are inefficient quenchers of $CO^\dagger$.

High $[O_2]/[CO]$ Regime

We assume that all reactions of O_2^* are important, but that all O_3 or oxygen atoms react to give CO_2, i.e. reactions 16 and 19 are negligible. Then Equation II can be rearranged to

$$2f''(\Phi\{CO_2\} - f'\Phi')^{-1} = 2(\Phi'')^{-1} = \frac{1 + k_{12}/k_9 + (k_{13} + k_{14})[O_2]/k_9[CO]}{\beta + k_{13}[O_2]/k_9[CO]} \quad \text{XI}$$

The left-hand side of Equation XI can be computed from the known quenching constants for $Hg(^3P_1)$ and $Hg(^3P_o)$ and the rate constant ratios already evaluated. The function β is dependent only on the total pressure (see Equation VII). Thus for a given total pressure, the right-hand side of the equation should be a constant $= (1 + k_{12}/k_9)/\beta$ at low $[O_2]/[CO]$, should change regularly as $[O_2]/[CO]$ increases, and should again be a constant $= (k_{13} + k_{14})/k_{13}$ at high $[O_2]/[CO]$ ratios. The appropriate plots are shown in Figure 6.

For values of $[O_2]/[CO]$ between 0.1 and 1 and at a total pressure of 500 torr, $(\Phi'')^{-1}$ is a constant. It rises to a plateau as $[O_2]/[CO]$ increases, but for $[O_2]/[CO]$ above 100 it increases once again. The behavior of $(\Phi'')^{-1}$ up to $[O_2]/[CO] = 100$ is consistent with the prediction of Equation XI, but deviation occurs for $[O_2]/[CO] > 100$. A decrease in $\Phi\{CO_2\}$, hence an increase in $(\Phi'')^{-1}$ must eventually occur as

$[O_2]/[CO] \rightarrow \infty$, since either reaction 16 or 19 or both will become important. Evidently reaction 16 or 19 becomes important at $[O_2]/[CO] = 100$. At lower total pressures $(\Phi'')^{-1}$ is still constant for $[O_2]/[CO]$ between 0.1 and 1, but it increases more rapidly with increasing $[O_2]/[CO]$ than at 500 torr, contrary to the prediction of Equation XI. It appears that at lower pressures the assumption that $R\{16\} + 2R\{19\}$ is negligible breaks down at lower $[O_2]/[CO]$. This is readily understandable if reaction 16 becomes important. If reaction 19 is important, it can be shown that $R\{19\}$ could increase or decrease with pressure depending on the values of the rate constants.

From the curves in Figure 6 at low $[O_2]/[CO]$, the three values of $2(\Phi'')^{-1} = (1 + k_{12}/k_9)/\beta$ are found to be 6.3, 5.3, and 4.4, respectively at 50, 100, and 500 torr total pressure. By adjusting the remaining parameters in Equation XI, the curves which best fit the data points in the applicable regions can be constructed. These theoretically computed curves are for values of $(k_{13} + k_{14})/(k_9 + k_{12}) = 0.20$ and $k_{14}/k_{13} = 12$, and they are shown as the solid lines in Figure 6. Both rate constant ratios have been obtained in previous studies. The value of 0.20 for $(k_{13} + k_{14})/(k_9 + k_{12})$ is identical to that found by Heicklen and Johnston.[2] The value of 12 for k_{14}/k_{13} lies within the previously reported range of 7-33.[1]

In the low $[O_2]/[CO]$, constant $(\Phi'')^{-1}$ region, expression XI reduces to

$$2(\Phi'')^{-1} = (1 + \frac{k_{12}}{k_9})(1 + k_{11}/k_{10}[M]) \qquad \text{XII}$$

Expression XII predicts that a plot of $2(\Phi'')^{-1}$ vs. $[M]^{-1}$ will be linear. This plot is presented in Figure 7. The intercept gives $k_{12}/k_9 = 3.25$

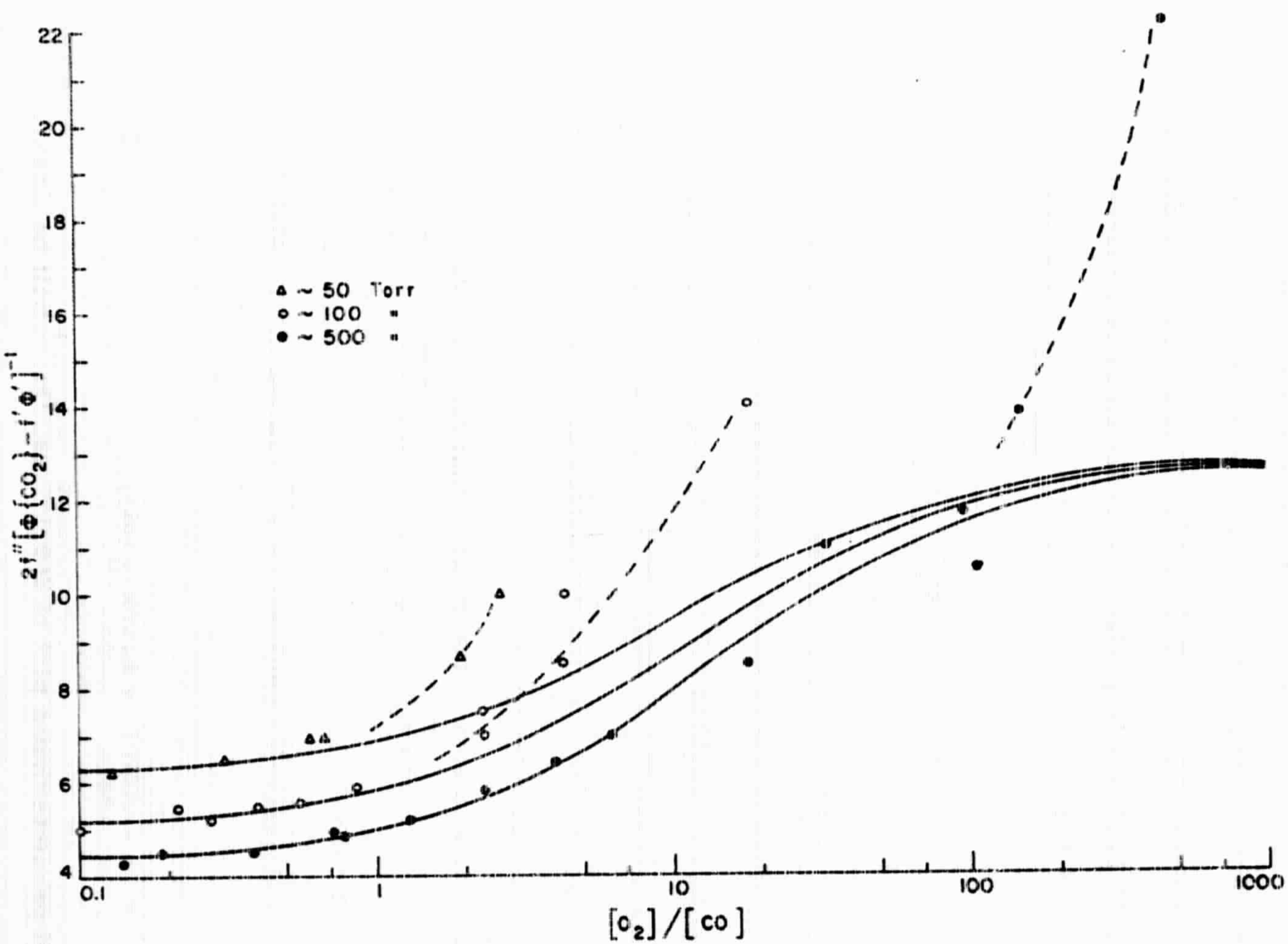


Figure 6

Plots of $2f''(\Phi\{CO_2\} - f'\Phi')^{-1}$ vs. $[O_2]/[CO]$ in the high $[O_2]/[CO]$ regime at ~ 50, 100 and 500 torr total pressure at 275°C. The solid lines are theoretically computed plots based on Equation XI with the adjusted parameters given in Table V. The dashed lines follow the trend of the experimental points.

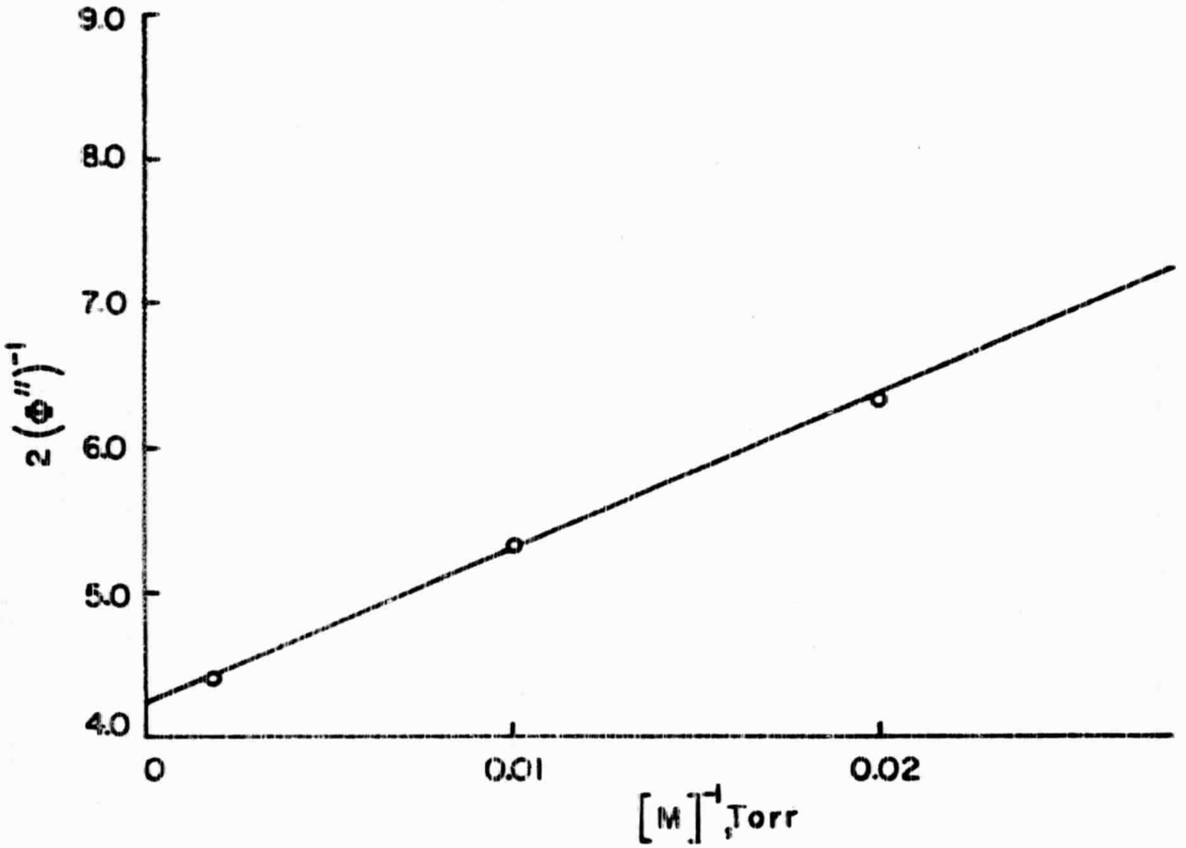


Figure 7

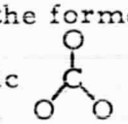
Plots of $2(\Phi'')^{-1}$ vs. $1/[M]$ in the region of low $[O_2]/[CO]$ at 275°C. The data points are taken from the intercepts of Figure 6.

and the slope gives $k_{11}/k_{10} = 25$ torr. The increase in $\Phi\{CO_2\}$ upon raising the total pressure by increasing $[O_2] + [CO]$ at constant $[O_2]/[CO]$ cannot be due to an increase in $[O_2]$ or $[CO]$, because if CF_4 is used to increase the total pressure the same effect is observed. The fact that $(\Phi'')^{-1}$ vs. $[M]^{-1}$ is linear argues against the importance of reaction 23.

$$CO_3 \rightarrow CO_2 + O \tag{23}$$

The recent study of CO_3 formation via reaction 24 by DeMore and Dede[8]

$$O(^1D) + CO_2 \rightarrow CO_3 \tag{24}$$

showed that CO_3 is formed only at pressures greater than 100 psi, indicating a lifetime of 10^{-11} to 10^{-12} sec. for the initially formed CO_3. Our result for $k_{11}/k_{10} = 25$ torr gives a lifetime for the CO_3 formed in reaction 9 as $\sim 10^{-7}$ sec., assuming a collisionally induced predissociation rate of 10^{11} $\underline{M}^{-1}$/sec. This is in sharp contrast to the results of Demore and Dede, in particular when one considers that reaction 9 is ~66 kcal/mole more exothermic than reaction 24, assuming the same CO_3 structure. We conclude that the CO_3 formed in reactions 9 and 24 must have different structures. Presumably the former is asymmetric OCOO, whereas the latter is the symmetric  molecule.

In the presence of TMP the mechanism predicts that for $[O_2]/[CO]$ radios sufficiently low (< 2) so that reactions 13 and 14 are unimportant, and for $[CO]/[TMP]$ ratios sufficiently low so that reaction 21 does not occur but sufficiently high to scavenge all the oxygen atoms, $\Phi\{CO_2\}$ should be reduced by a factor of 2 from the value in the absence of TMP and $\Phi\{CO_2\} = \Phi\{E\} + \Phi\{A\}$. Figure 1 and the data in Table III show that for the runs with [TMP] ~ 1 torr these expectations are approximately fulfilled. $\Phi\{CO_2\}$ is not reduced exactly by a factor of 2 and $\Phi\{CO_2\}$ is somewhat larger than $\Phi\{E\} + \Phi\{A\}$ because only 70-80% of the oxygen atoms are scavenged by TMP when [CO]/[TMP] = 400, as can be shown using the relative rate constant for reactions 20 and 15 (k_{20}/k_{15} = 800 at 548°C).[10] The above quantum yield relationships show that for each CO_2 molecule produced one oxygen atom is also formed; therefore reactions 25 and 26 cannot be important.

$$CO_3 + O_2 \rightarrow CO_2 + O_3 \qquad (25)$$

$$CO_3 + CO \rightarrow 2\,CO_2 \qquad (26)$$

For the runs with [TMP] > 3 torr, $\Phi\{E\} + \Phi\{A\} > \Phi\{CO_2\}$ and $\Phi\{CO_2\}$ drops more than a factor of 2 from the value in the absence of TMP. It is clear that at these lower [CO]/[TMP] ratios the quenching of O_2^* by TMP takes place. From the variation $\Phi\{CO_2\}$ as a function of the [CO]/[TMP] ratio an approximate value for $(k_9 + k_{12})/k_{21}$ can be calculated from

$$\Phi\{CO_2\} = \Phi'''\{CO_2\}\frac{k_{21}[TMP]}{k_{21}[TMP]+(k_9+k_{12})[CO]} + \Phi_o\{CO_2\}\frac{(k_9+k_{12})[CO]}{k_{21}[TMP]+(k_9+k_{12})[CO]} \qquad \text{XIII}$$

where $\Phi'''\{CO_2\}$ = 0.050 is the quantum yield of CO_2 in the presence of TMP alone and $\Phi_o\{CO_2\}$ is the quantum yield of CO_2 when reaction 21 is unimportant (the runs at low [TMP], but otherwise comparable conditions). From the runs with [TMP] = 10 and 22 torr and the appropriate values of $\Phi_o\{CO_2\}$, the average value for $(k_9 + k_{12})/k_{21}$ is calculated to be 0.06. Combining this value with $(k_{13}+k_{14})/(k_9+k_{12}) = 0.20$ gives $(k_{13}+k_{14})/k_{21} =$ 0.012.

The relative reactivity of O_2^* with TMP measured in this investigation, $(k_{13} + k_{14})/k_{21} = 0.012$, lies between the values for C_2H_4 and C_3F_6 measured by Heicklen and Johnston.[2] The relative reactivities based on $O_2 = 1$ are the following: $C_3F_6 = 5.6$, TMP = 83, $C_2H_4 \geq 4700$. Thus the extent of fluorination strongly influences the reactivity of the olefin towards O_2^*.

In the earlier study of the reactivity of various gases with O_2^*,[2] Heicklen and Johnston observed that CF_4 had no effect, but that N_2 behaved in an unusual manner which was not explained. In this investigation we find that N_2 does not increase $\Phi\{CO_2\}$ in the high $[O_2]/[CO]$ regime as much as expected. The effect observed by Heicklen and Johnston was much more pronounced, but agrees qualitatively with the anomalous pressure effect observed in this study. The most reasonable explanation of the earlier results and those obtained in this work is that N_2 deactivates O_2^* to a state of different reactivity.

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