

THE CHLORINE-ATOM INITIATED AND Hg 6(³P₁)-PHOTOSENSITIZED OXIDATION OF CH₂CCl₂

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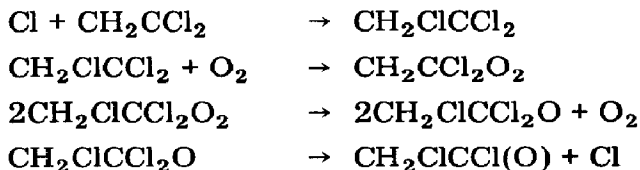
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Summary

The chlorine-atom initiated and Hg 6(³P₁)-photosensitized oxidation of CH₂CCl₂ was studied at 32 °C. In both cases a long chain process was involved in which the major product was CH₂ClCCl(O), and the minor product was CCl₂O. In the chlorine-atom initiated study, CO was not an initial product, but appeared as a minor secondary product suggesting CHClO as a precursor. In the Hg-photosensitized study, minor amounts of CO appear to be an initial product.

The chain steps in both studies are:

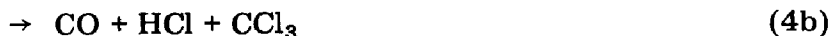


In the chlorine-atom initiated oxidation $-\Phi\{\text{CH}_2\text{CCl}_2\} = \Phi\{\text{CH}_2\text{ClCCl(O)}\} = 172$ independent of $[\text{CH}_2\text{CCl}_2]$, $[\text{O}_2]$, or I_a . In the Hg-photosensitized oxidation, both $-\Phi\{\text{CH}_2\text{CCl}_2\}$ and $\Phi\{\text{CH}_2\text{ClCCl(O)}\}$ were proportional to $[\text{CH}_2\text{CCl}_2]$, but independent of I_a and $[\text{O}_2]$ (for $[\text{O}_2]/[\text{CH}_2\text{CCl}_2] < 1.8$). Thus the termination steps are different in the two systems, and various possibilities are discussed.

Introduction

The free-radical oxidation of CH₂CCl₂ apparently has not been studied previously. However, for C₂Cl₄ both chlorine-atom initiated [1 - 5] and Hg photosensitized [6] oxidation have been studied. Likewise for C₂HCl₃ the chlorine-atom initiated [7, 8] and Hg photosensitized [9] oxidation have been studied. The results for C₂Cl₄ and C₂HCl₃ were analogous. The oxidation was a long free-radical chain process, and for C₂HCl₃, the chain steps are:

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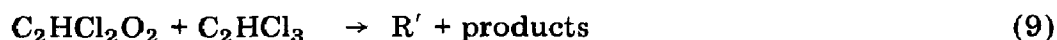
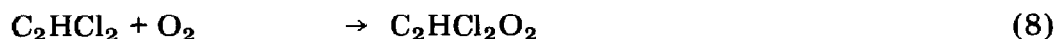
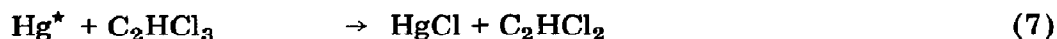


where R is either $\text{CHCl}_2\text{CCl}_2$ or CCl_3CHCl . Reaction (4a) occurs when RO is $\text{CHCl}_2\text{CCl}_2\text{O}$, and reaction (4b) occurs when RO is CCl_3CHClO .

The rate laws were different for chlorine-atom initiation and Hg photo-sensitization. For chlorine atom initiation, the chain length was independent of all reaction parameters (at least for sufficiently high O_2 pressures). Initiation and termination were, respectively:



With Hg-sensitization, the chain length was proportional to the olefin pressure. The initiation steps proposed were:



where R' is either $\text{C}_2\text{H}_2\text{Cl}_3$ or C_2HCl_4 . The termination would then be first order in $\text{C}_2\text{HCl}_2\text{O}_2$:



The mechanistic details of reaction (10) are not clear. It is needed to explain the rate law, and possibly occurs on the wall of the reaction vessel.

As part of a continuing study on chloro-olefin oxidation, we have extended our studies to CH_2CCl_2 . The results of the free-radical oxidation of that molecule are presented here.

Experimental

The experimental procedure has been described elsewhere [5, 6, 10]. The T-shaped reaction vessel was situated in the sample beam of a Beckman IR-10 spectrometer for continual analysis of CH_2CCl_2 removal and $\text{CH}_2\text{ClCCl}(\text{O})$ formation by their respective bands at 1640 and 1850 cm^{-1} . CCl_2O was analyzed after the radiation was discontinued, because its infrared bands were masked by the other species present. The CCl_2O was isolated for the analysis in the fraction volatile at -90°C but condensable at -196°C . CO analysis was by gas chromatography after the irradiation was terminated.

Results

In both the chlorine-atom initiated and Hg-photosensitized oxidation a long chain process is involved. The major product is $\text{CH}_2\text{ClCCl}(\text{O})$, and its quantum yield of formation, $\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\}$, is essentially equal to the quantum yield of CH_2CCl_2 consumption, $-\Phi\{\text{CH}_2\text{CCl}_2\}$. In both studies minor amounts of CCl_2O and CO are also found. There was no evidence for CH_2O , $\text{CHCl}_2\text{CH}(\text{O})$, HCl or CHClO production. For CHClO the upper limit for its quantum yield is 1.0 in the chlorine-atom initiated oxidation.

The quantum yields for several runs in the chlorine-atom initiated oxidation are shown in Table 1. $-\Phi\{\text{CH}_2\text{CCl}_2\} = \Phi\{\text{CH}_2\text{ClCCl}(\text{O})\} = 172$ independent of a change in $[\text{CH}_2\text{CCl}_2]$ by a factor of 5.6, $[\text{O}_2]$ by a factor of 100, or the absorbed intensity, I_a , by a factor of 7.5. The values for $\Phi\{\text{CCl}_2\text{O}\}$ show considerable scatter but are about 2. Initial quantum yields of CO are immeasurable ($\Phi\{\text{CO}\} < 0.2$), but in one run which was allowed to stand for 1 h after irradiation before analysis, $\Phi\{\text{CO}\} \sim 1$.

The reaction proceeds proportionately with irradiation time, as can be seen from Figs. 1 and 2 which are plots, respectively, of the intensity-normalized CH_2CCl_2 consumption and $\text{CH}_2\text{ClCCl}(\text{O})$ production *vs.* irradiation time. Both plots are linear, and all the runs can be represented by the same straight line which gives a slope (*i.e.* quantum yield) of 172 in both plots. Possibly the two runs at highest O_2 pressure show some fall-off at long conversions, but this is minor, if indeed it is real.

The results for the Hg-photosensitized oxidation of CH_2CCl_2 are shown in Table 2. For these experiments, $[\text{CH}_2\text{CCl}_2]$ was varied by a factor of 13, $[\text{O}_2]$ by a factor of 44, and I_a by a factor of 12.5. During the runs, the radiation was periodically interrupted and the cell shaken to eliminate the inhibition that occurs if shaking is not done. Here the quantum yields of the chlorinated compounds are much smaller than for the chlorine-atom initiated oxidation. Also $-\Phi\{\text{CH}_2\text{CCl}_2\}$ and $\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\}$ increase with $[\text{CH}_2\text{CCl}_2]$, but $\Phi\{\text{CO}\}$ and $\Phi\{\text{CCl}_2\text{O}\}$ are independent of parameters and are each between 0.5 and 1.0.

Figure 3 shows log-log plots of $-\Phi\{\text{CH}_2\text{CCl}_2\}$ and $\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\}$ *vs.* $[\text{CH}_2\text{CCl}_2]$. The plots can be fitted by lines of slope 1.0 indicating that the quantum yields are proportional to the CH_2CCl_2 pressure. The two runs at highest $[\text{O}_2]/[\text{CH}_2\text{CCl}_2]$ ratio lie noticeably below the line that best fits the other points, suggesting that O_2 has an inhibiting effect.

Discussion

The main chain sequence certainly must be:

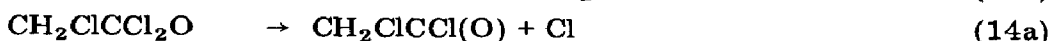
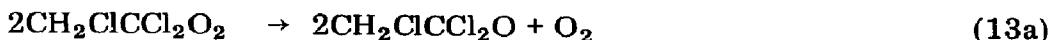


TABLE 1

The chlorine-atom sensitized oxidation of CH_2CCl_2 at 32 °C

Symbols for Figs.	$[\text{CH}_2\text{CCl}_2]$ (Torr)	$[\text{O}_2]$ (Torr)	$[\text{Cl}_2]$ (Torr)	I_a^a (mTorr/s)	$-\Phi\{\text{CH}_2\text{CCl}_2\}$	$\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\}$	$\Phi\{\text{CCl}_2\text{O}\}$
○ ^b	2.40	22.8	1.7	0.26	188	184	—
▲	3.69	4.94	1.73	0.26	190	175	2.6
■ ^c	3.72	13.25	1.69	0.25	167	163	—
□	3.06	18.5	5.30	0.63	166	173	2.1
●	3.81	189	1.73	0.26	167	175	2.6
◐ ^d	3.30	498	1.91	0.28	167	173	—
◑ ^d	5.82	15.6	10.5	1.25	166	173	—
◒ ^d	7.30	14.8	1.4	0.166	174	168	—
○ ^d	8.90	20.0	5.3	0.631	178	178	1.25
△	13.50	11.5	5.23	0.622	181	193	—

^a Assuming quantum yield of oxidation of C_2Cl_4 as 300 at high O_2 pressure.^b 0.45 Torr of HCl also present.^c $\Phi\{\text{CO}\} \sim 1$. Analysis for CO made 1 h after termination of irradiation.^d $\Phi\{\text{CO}\} < 0.2$.

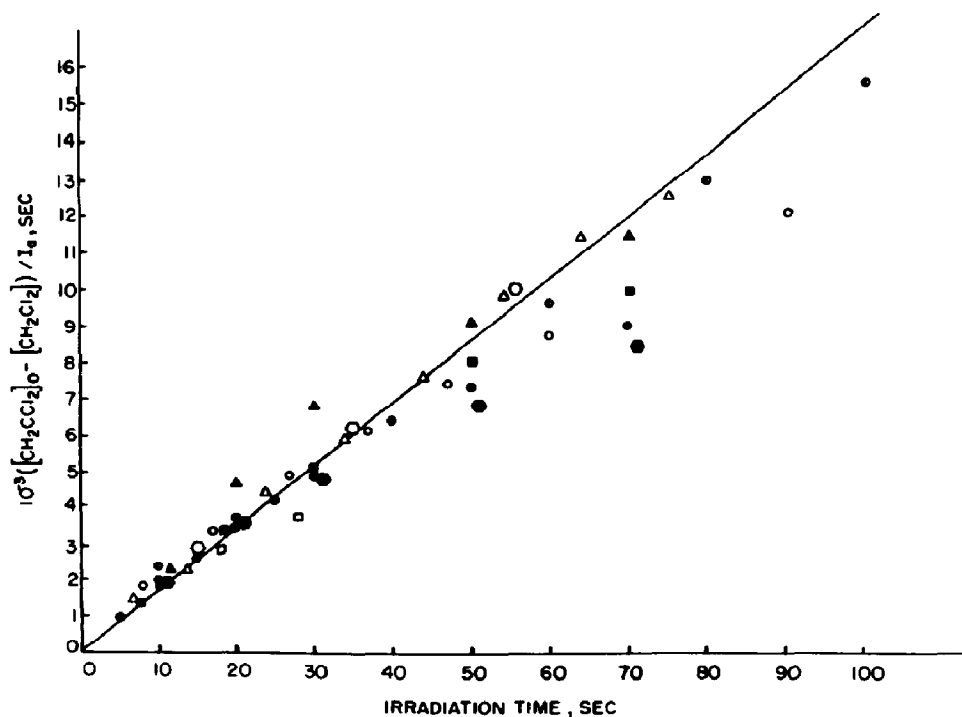


Fig. 1. Plot of CH_2CCl_2 consumption divided by I_a vs. irradiation time in the chlorine-atom sensitized oxidation of CH_2CCl_2 at 32°C . The key to the symbols is given in Table 1.

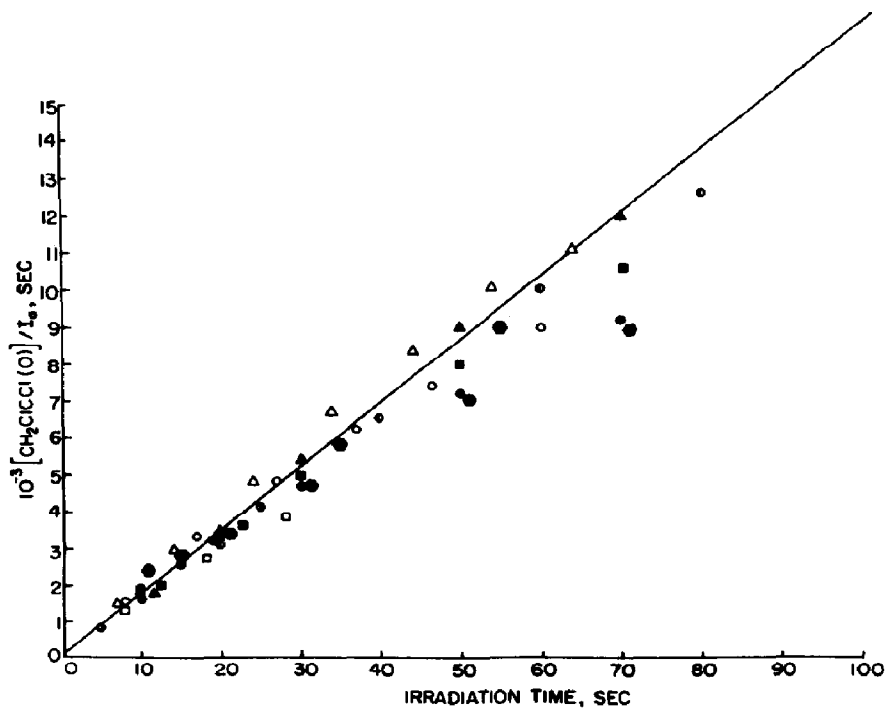


Fig. 2. Plot of $[\text{CH}_2\text{ClCCl}(\text{O})]/I_a$ vs. irradiation time in the chlorine-atom sensitized oxidation of CH_2CCl_2 at 32°C . The key to the symbols is given in Table 1.

TABLE 2
The Hg 6(³P)-photosensitized oxidation of CH₂CCl₂

[CH ₂ CCl ₂] (Torr)	[O ₂] (Torr)	I _a ^a (mTorr/s)	Irradiation time (s)	-Φ{CH ₂ CCl ₂ } ^b	Φ{CH ₂ ClCCl(O)} ^b	Φ{CO} ^c	Φ{CCl ₂ O} ^c
1.54	0.8	0.12	1300	8.0	7.1	0.7	0.7
1.93	1.2	0.95	126	10.3	13.4	0.5	0.7
2.10	1.75	0.20	700	10.8	10.0	0.7	0.8
4.44	2.2	1.02	150	24.0	25.0	0.5	0.9
5.00	1.22	0.91	150	27	26	0.7	1.0
6.01	3.7	0.37	500	27	30	0.5	0.7
7.8	5.0	0.21	1130	33	29	1.0	0.7
8.87	35.2	1.5	200	28	26	—	0.5
8.95	10.0	1.5	150	47	46	0.5	0.8
9.05	5.0	1.45	202	48	43	0.4	0.8
9.73	19.1	1.45	260	35	26	—	0.4
15.1	7.9	1.49	220	72	56	0.4	0.8
20.0	14.1	0.95	—	—	60	—	—

^a I_a at the beginning of the run.

^b Based on initial rates.

^c Computed from final values of CO and CCl₂O.

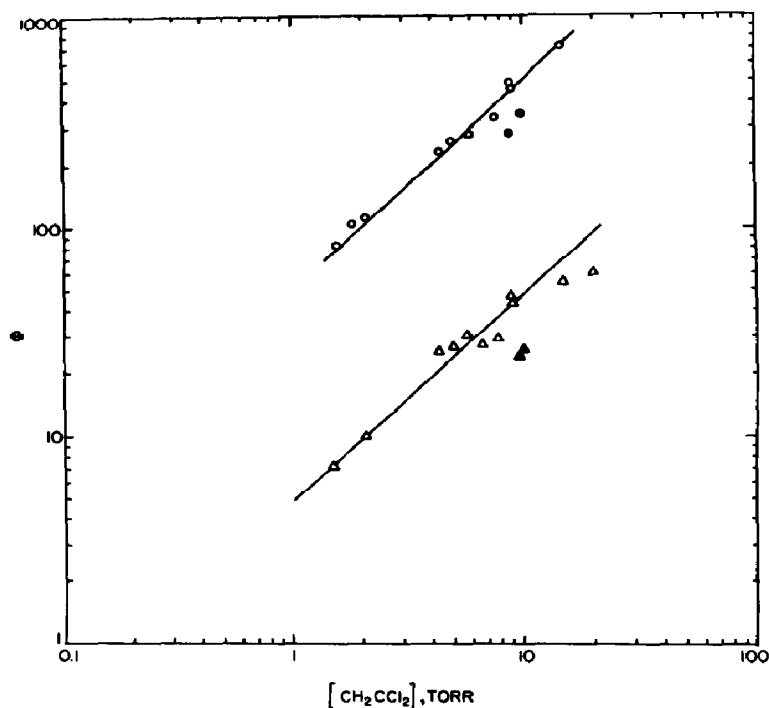


Fig. 3. Plot of $-\Phi\{\text{CH}_2\text{CCl}_2\}$ (\circ , \bullet) or $\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\}$ (Δ , \blacktriangle) vs. $[\text{CH}_2\text{CCl}_2]$ in the Hg-photosensitized oxidation of CH_2CCl_2 at 32°C . The plot for $-\Phi\{\text{CH}_2\text{CCl}_2\}$ has been raised by a factor of 10 for clarity. Δ , \circ , $[\text{O}_2]/[\text{CH}_2\text{CCl}_2] < 1.8$; \bullet , \blacktriangle , $[\text{O}_2]/[\text{CH}_2\text{CCl}_2] > 1.8$.

For every CH_2CCl_2 consumed one molecule of $\text{CH}_2\text{ClCCl}(\text{O})$ is produced. A possible minor route which might compete with reaction (11a) is:

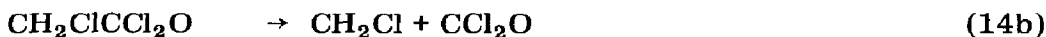
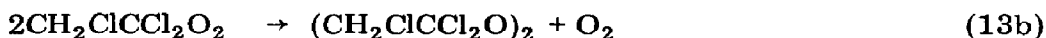


The CCl_3CH_2 radical would oxidize as follows:



The upper limit to $k_{11b}/k_{11a} = \Phi\{\text{CCl}_2\text{O}\}/\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\} \sim 0.01$. We found no CH_2O , but we could have missed the small amount produced.

In the chlorine-atom sensitized oxidation, the initiation occurs *via* reaction (6). Since the quantum yields are insensitive to the reaction parameters, there are only two possible terminating reactions:



In a separate study [11], we have shown that CH_2Cl always oxidizes to CHClO in a non-chain process. Thus both reaction (13b) and (14b) are terminating steps.

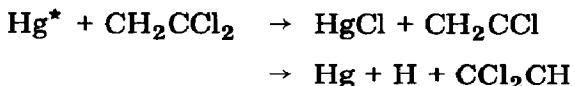
If reaction (13b) is the sole terminating step then $k_{13a}/k_{13b} = 86$. Furthermore if $(\text{CH}_2\text{ClCCl}_2\text{O})_2$ does not decompose, then $k_{11b}/k_{11} \sim 0.01$.

However, if $(\text{CH}_2\text{ClCCl}_2\text{O})_2$ decomposes, presumably to give CCl_2O and CHClO , then reaction (11b) must be even less important, because CCl_2O is produced *via* termination.

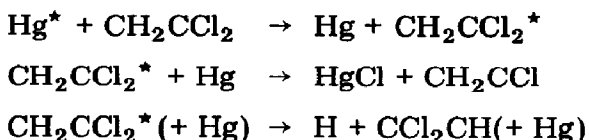
On the other hand, if reaction (14b) is the sole termination step then $k_{14a}/k_{14b} = 86$ and reaction (11b) does not occur at all, because all the CCl_2O comes from the termination ($\Phi\{\text{CCl}_2\text{O}\} = 2.0$). Of course, if reaction (11b) does not occur at all, then $\Phi\{\text{CCl}_2\text{O}\}$ should equal $\Phi\{\text{CHClO}\}$ by either termination mechanism. Our results indicate that $\Phi\{\text{CCl}_2\text{O}\} \sim 2$ and $\Phi\{\text{CHClO}\} \leq 1$. (Presumably $\Phi\{\text{CHClO}\} \sim 1$, since for the run that was allowed to stand before CO analysis, $\Phi\{\text{CO}\} \sim 1$. The CO comes from the thermal decomposition of CHClO [12].) Thus our very tentative conclusion is that reaction (11b) occurs to some extent, and that termination leads to $(\text{CH}_2\text{ClCCl}_2\text{O})_2$ part, but not all, of the time.

In the Hg-photosensitized oxidation the initiation and termination possibilities are more numerous. The possibility that Hg-photosensitization gives exclusively molecular elimination of HCl can be discarded, since then there would be no chain process. We can also discard the possibility that the double bond is ruptured to produce CH_2 and CCl_2 . Initiation by CCl_2 radicals does give the same products, but the rate law is intensity-dependent [10], contrary to our observations here (CH_2 reacts with O_2 to give HCOOH or $\text{H}_2\text{O} + \text{CO}$, so it would play no role).

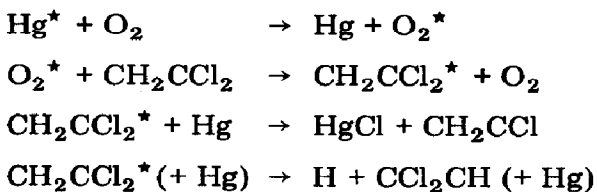
Thus, as in the case with C_2Cl_4 and C_2HCl_3 , Hg-photosensitization leads to the formation of free radicals. There are two possible radicals to consider, CH_2CCl or CCl_2CH . They could be produced by several routes, but the kinetics are indistinguishable. Among the possibilities are:



or



or

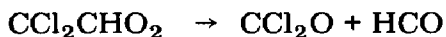


In any event either CH_2CCl or CCl_2CH must be produced. In order to give the observed rate law, *i.e.* $\Phi\{\text{CH}_2\text{ClCCl}(\text{O})\}$ being proportional to $[\text{CH}_2\text{CCl}_2]$, these radicals, designated R'' , must obey the following kinetics:



Reaction (16) probably occurs on the wall and is the dominant reaction for $R''O_2$. Reaction (17) is the chain-initiating step and occurs 4 - 40% of the time (the chain lengths in the Hg-photooxidation are 4 - 40% of those in the chlorine-atom initiated oxidation). Thus the stable products of reaction (17), whatever they might be (glyoxals, HCl, CO), are unimportant.

Reaction (16), on the other hand, must account for some of the CCl_2O and CO produced, since the sum of their quantum yields exceeds 1.0. It is not at all clear how reaction (16) proceeds, since ultimately it must involve another free radical to lead to stable products. However, speculative possibilities are:

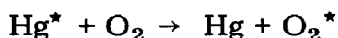


where HCO terminates *via*:



It is interesting to note that CH_2CClO_2 does not give CCl_2O . Since $\Phi\{CCl_2O\}$ is independent of $[CH_2CCl_2]$, it must come mainly from termination, and CCl_2CHO_2 would be the more important $R''O_2$ radical.

Finally we point out that at high values of $[O_2]/[CH_2CCl_2]$, the quantum yields in the Hg-photosensitization are reduced because of the reactions:



Acknowledgement

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