



COMMENT

Comment on "Degradation of polychlorinated dibenzo-*p*-dioxin and dibenzofuran contaminants in 2,4,5-T by photoassisted iron-catalyzed hydrogen peroxide" by J. J. PIGNATELLO and L. Q. HUANG, *Wat. Res.* **27**, 1731-1736 (1993).

This is an excellent piece of work done by the author. The data presented in this paper is highly pertinent to the researcher in the field of environmental pollution. As the work is very much interesting it would be highly appreciated if the author elaborate some of the points illustrated here.

(1) In order to determine the fate of polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) contaminants in the herbicide, 2,4,5-trichlorophenoxyacetic acid the author has used $\text{Fe}(\text{ClO}_4)_3$ as catalyst in a buffer medium of pH - 2.75 (adjusted with HClO_4) but interpreted the results exclusively as the catalytic effect of Fe. Thus it is not clear why ferric perchlorate salts was used as catalyst for the degradation process. Perchlorate itself acts as an oxidising agent as is evident from its electrode potential (Weast and Astle, 1982):

	Red. Pot.
$\text{ClO}_4 + 4\text{H}_2\text{O} + 8e \rightarrow \text{Cl}^- + 8\text{OH}^-$	0.56
$\text{ClO}_4 - 8\text{H}^+ + 8e \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$	1.37
$\text{Fe}^{+3} + e \rightarrow \text{Fe}^{+2}$	0.77
$\text{Fe}^{+3} + e \rightarrow \text{Fe}(\text{HClO}_4)$	0.75

Thus the results reproduced as the catalytic effect of Fe may be considered as the combined effect of Fe and perchlorate ions

(2) It appears that H_2O_2 was used in the reaction medium to reinforce the oxidative degradation process. But the impact of H_2O_2 on degradation of PCDD and PCDF would have been observed exclusively had there been no perchlorate ions in the reaction medium. It would be rather interesting if the author could present some data in that respect.

(3) Since the degradation study was carried out by photoassisted iron catalyzed hydrogen peroxide it is most likely that the reaction mechanism followed the path of free-radical formation (Koshika *et al.*, 1987). If that is so, it can be detected in the mass spectrum of each of the analyses (Smith and Cristol, 1966; Budzikiewicz, 1967). Otherwise, the free-radical formation can be detected by electron spin resonance spectra. This is highly important to illustrate the observed variation in the concentration of different congeners of PCDDs and PCDFs (Table 1).

(4) It is mentioned in the results and discussion (page 1733, 1st para) that the extraction of triplicate samples of aqueous 2,4,5-T gave relative standard deviation of individual peaks ranging from ± 2 to 71 with a mean $\pm 44\%$. The author claimed that the range is not unusual for ultratrace analysis of these compounds. But the point is that with such a wide range of variation in the standard deviation it is quite difficult to evaluate distinctly the effect of $\text{Fe}/h\nu$, $\text{Fe}/\text{H}_2\text{O}_2$ and $\text{Fe}/\text{H}_2\text{O}_2/h\nu$ on degradation process. The author has mentioned in the experimental section (p. 1732, para 4, line 7) that internal standard was used as routine analysis for determination of recovery but did not specify the name of the internal standard. This is an important step for evaluation of the data. The author should justify exclusively for wide range of standard deviation otherwise the interpretation of the results does not stand to be very authentic. Statistically it is unacceptable. There must be some valid reasons for which standard deviation was so high.

(5) A critical examination of the results of the analysis (Table 1) shows very interesting features. Concentration of 2378-TCDD (peak no. 2) was found to be increased unusually to 350 (irradiation control). Proper justification should be provided to elucidate such unusual increase in concentration. It is already mentioned that in a study of photolysis of 2,4,5-T itself none of the most toxic dioxin (2,3,7,8-TCDD) was produced (see introduction, last para) (Crosby and Wong, 1973). In this regard, the free radical mechanism of such synthesis is most likely to be feasible. Similarly is the case with 12468- and 12479-pentachloro-dibenzo-dioxins (peak no. 3). The concentration of these compounds increased unusually to 230% ($\text{Fe}/h\nu$). Is it because

Table 1. Results of degradation of PCDD and PCDF impurities in reagent grade 2,4,5-T

Peak	Initial concentration (pg/g)	Percent remaining				
		Dark control	Irradiation control	Fe/hv	Fe/H ₂ O ₂	Fe/H ₂ O ₂ /hv
<i>Dioxins</i>						
1. 1379	280	130	88	0	0	0
2. 2378	1590	110	350 ^a	63	7	0
total tetra	1870	110	310 ^a	54	6	0
3. 12468, 12479	1020	180	—	230 ^a	13	7
4. 12368	700	160	110	29	4	0
5. 12379	370	130	120	13	0.4	0
total penta	2090	160	110	120 ^a	8	4
6. 124679, 124689	740	160	—	0	4 ^b	0
7. 123468	2890	160	150	5	7	0
8. 123679, 123689	2940	150	160	10	5	0
9. 123478	220	130	160	14	2	0
10. 123678	1040	100	140	12	2	0
11. 123789, 123467	600	150	170	24	3	0
12. 1234679	2530	180	170	36	11	0
13. 1234678	3220	150	170	35	11	0
<i>Furans</i>						
14. 2468	960	150	100	28	4	0
15. 1379, 1367, 1348, 1248	2020	170	160	37	3	0
16. 1469, 1678, 1234	600	150	130	36	5	0
17. 3467, 1269	80	100	140	86 ^a	10	8
18. 13678 ^a	33	150	0	0	16 ^b	14
19. 12368, 12478, 13478, 13467, 12467	1610	200	450 ^a	140	0	0
20. 23469, 14678, 13479	1290	130	120	27	0	0
21. 23468, 12347, 12346, 12469	970	170	150	27	3	0
22. 12348	510	160	100	21	9	0
23. 23467, 12489	120	60	170 ^a	74 ^a	20	9
total penta	4500	170	240 ^a	69	2	0.3
24. 134678, 124678	1350	150	—	15	6	0
25. 123478, 123467	920	140	130	16	13	3
26. 123678	1290	140	80	4	12 ^b	0.2
27. 123489	48	120	170	0	18 ^b	11
total hexa	3610	150	100	11	10	0.9
28. 1234678	660	140	160	33	12	4
29. 1234679	34	130	170	27	0.7	0
total hepta	694	140	160	35	11	4
30. octachloro	460	160	150	63	34	34

^aUnusual increase in concentration. ^bUnusual formation of PCDD and PCDF.

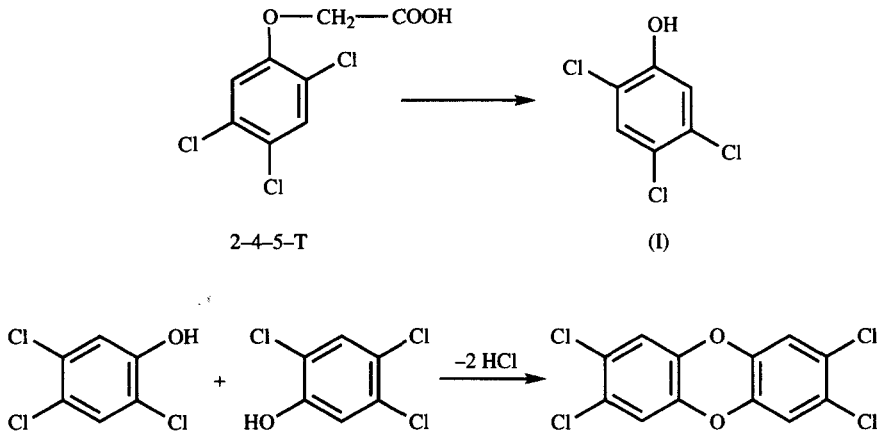
of formation of these compounds by photolytic reaction in presence of Fe(ClO₄)₃? The concentration of total pentachloro-dibenzo-dioxins (peak no. 5) was increased to 120% by treatment with Fe/hv posing a similar problem. Interestingly, 124679 and 124689-hexachloro-dibenzo-dioxins (peak no. 6) were completely degraded while 4% of their residues still remain even after treatment with Fe/H₂O₂. This has clearly indicated the action of photon in presence of Fe(ClO₄)₃. In the case of all other dioxin compounds there is gradual decrease in the residue levels. A proper illustration in this regard would be useful to highlight the importance of the use of hydrogen peroxide. Moreover, if the low percentage of residues of dioxin remaining after treatment with Fe(ClO₄)₃/hv is ignored for wide range of standard deviation of extraction, then the impact of hydrogen peroxide on degradation of dioxins (see columns 4 and 5, Table 1) cannot be justified. The author should clarify such variation in the concentration levels of different congeners of PCDD.

(6) In the case of furans, certain amount of undegraded compounds remain after treatment with Fe/H₂O₂/hv (e.g. peak no. 17, 18, 23, 27, 34) whereas 13678-pentachloro and 123489-hexachloro-dibenzo-furan were found to be completely degraded by treatment with Fe/hv only. Such an anomaly in the results should be explained with proper justification. An unusual increase in the concentration (see Table 1) of peak no. 19 in different stages (dark control, irradiation control and Fe/hv) is of immense interest from the point of view of reaction mechanisms. This could probably be due to formation of the furans by irradiation of degraded molecule and 2,4,5-trichlorophenoxide radical (obtained from 2,4,5-T) or catalytic effect of Fe/hv. The impact of H₂O₂ on these compounds was indicated by their complete degradation. But the results did not show the same implication in the case of another furan (peak no. 27). On the contrary, the effect of Fe/hv was found to be much more pronounced.

The variation in the concentration of the residues of undegraded congeners of PCDDs and PCDFs may be explained by careful examination of their structures.

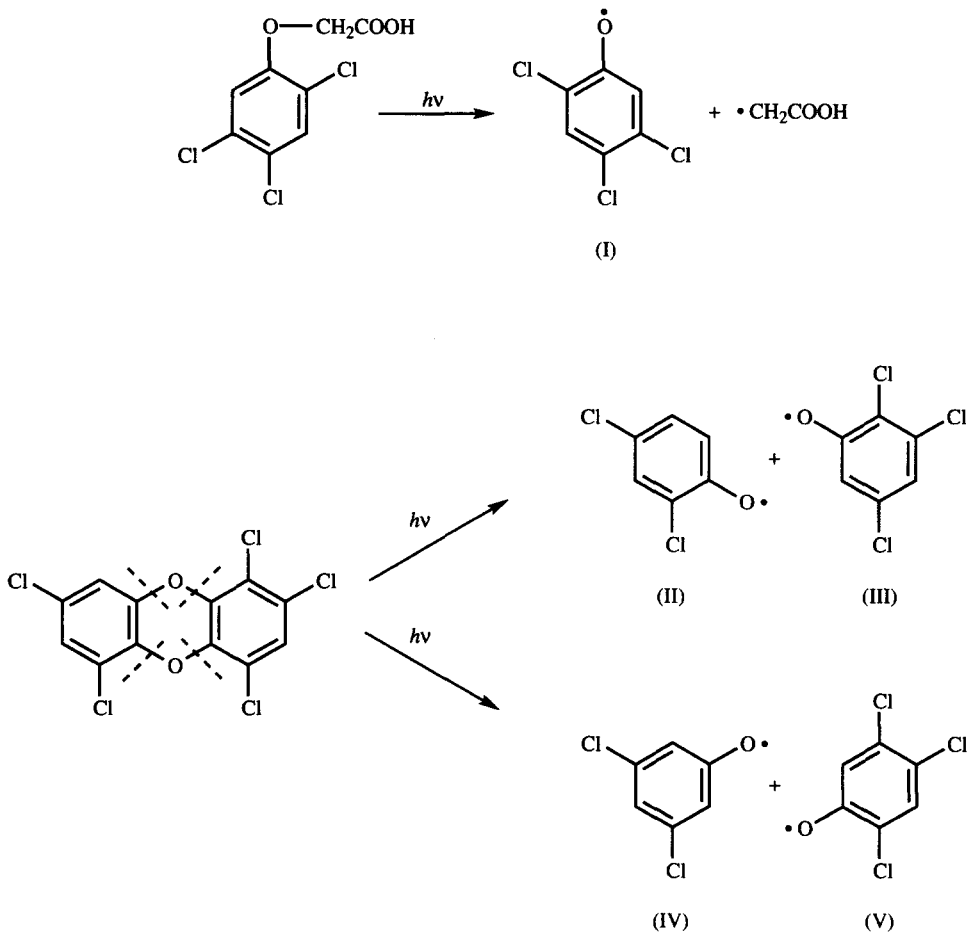
By applying the rule of symmetry and molecular orbital theory it is possible to differentiate the polarity of each of the congeners (Eliel, 1962; Ruzo *et al.*, 1975; Streitwieser Jr, 1961). In fact, dechlorination of each

of the congeners is greatly influenced by the polarity of the molecule. Thus it may be noted that both the compound 1379 (peak no. 1) and 2378 (peak no. 2) have the molecular symmetry but the latter may probably be produced by irradiation of trichlorophenol or degraded molecule. Considering the inductive effect, electromeric effect and mesomeric effect of chlorine atom it appears that 2378-tetrachloro-dibenzo dioxin is more stable than the other congener (i.e. 1379).

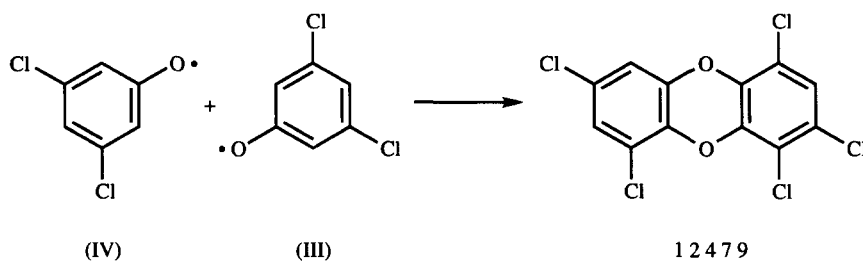
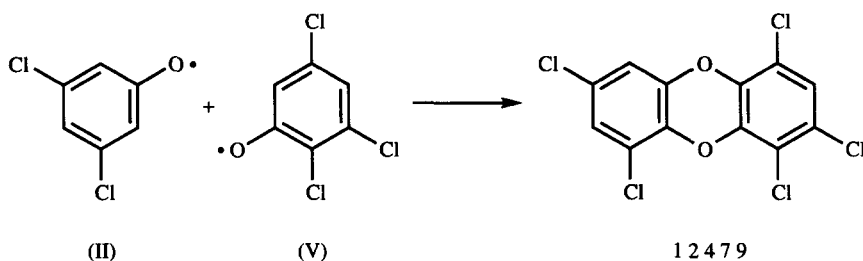
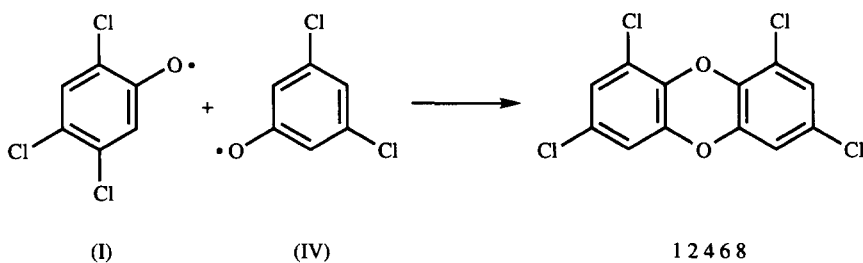
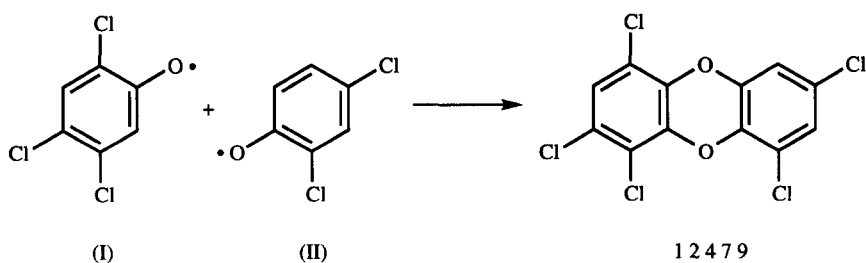


Scheme 1

In the case of 12468 and 12479 (peak no. 3) the increase in concentration of dioxin may probably be because of the following intermolecular oxidative reaction as illustrated below:



Scheme 2



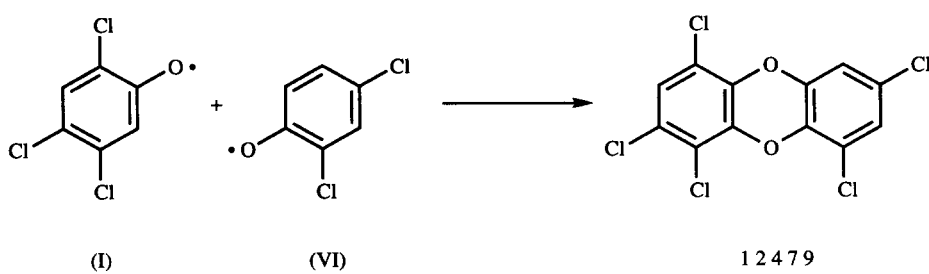
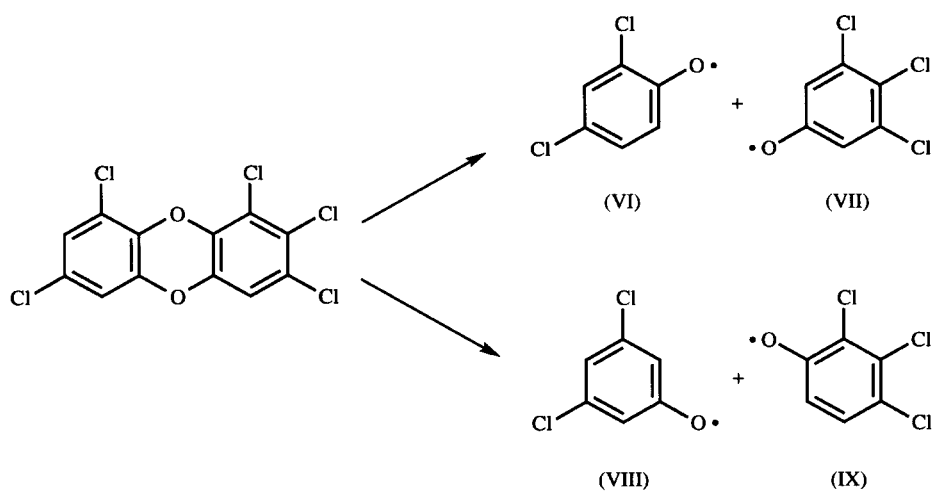
Scheme 3

In the case of 12379 (peak no. 5) the concentration is increased to 120% by irradiation control. This may probably be due to reproduction of dioxin by intermolecular interaction between the degradation product (VI, VII, VIII, IX) and 2,4,5-trichloro phenoxy radical obtained by photolysis of 2,4,5-T.

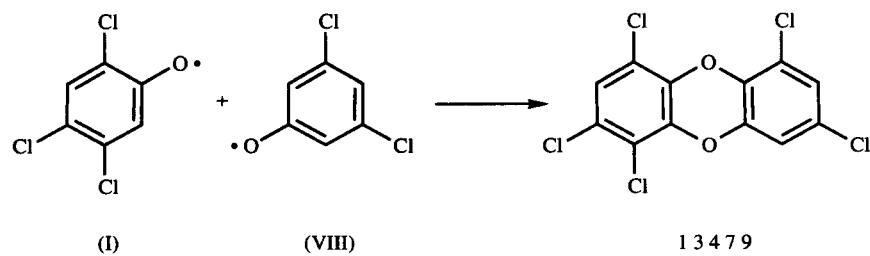
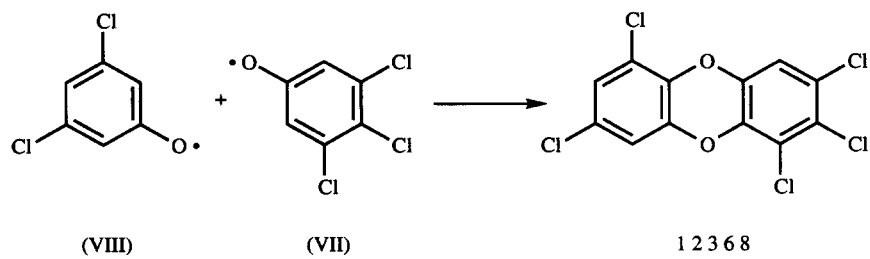
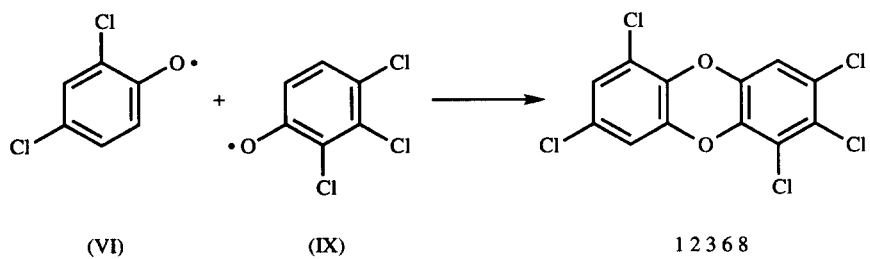
The 4% of dioxin compounds (124679, 124689, peak no. 6) remaining after treatment with $\text{Fe}/\text{H}_2\text{O}_2$ could probably be due to stability of the compound having molecular symmetry. However, the effect of photon in presence of $\text{Fe}(\text{ClO}_4)_3$ appears to be prominent.

It may be observed that because of molecular dissymmetry different congeners of PCDD and PCDFs are of different polarities eventually facilitating the degradation process.

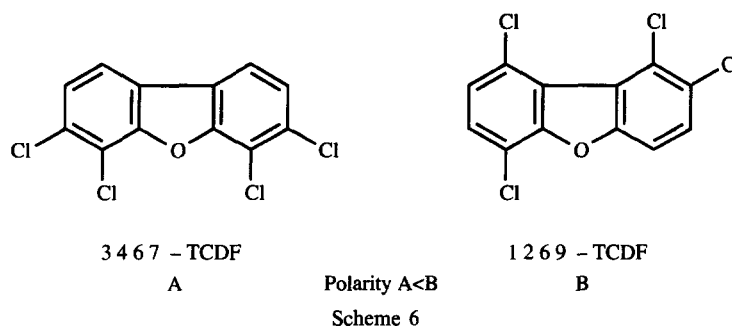
In the case of furans there was substantial amount of residues of TCDF (peak no. 17) remaining after treatment with $\text{Fe}/h\nu$. Such a high level of residues may be attributed to molecular symmetry of the two compounds.



Scheme 4



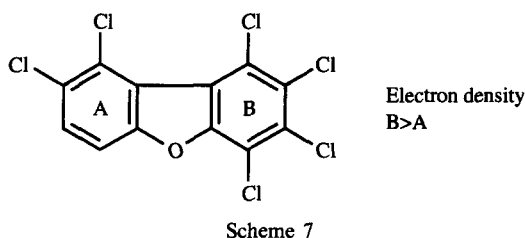
Scheme 5



Thus it is most likely that there should have been two well defined distinct peaks in the mass spectrum. The author should throw some light in this respect.

Surprisingly, 13678-pentachloro-dibenzo-furan (peak no. 18) is completely degraded by irradiation control and also Fe/hv. The same thing did not occur in all the other cases. The author is desired to enlighten the possible reasons for such differences.

It is very interesting that 123489-hexachloro-dibenzo-furan (peak no. 27) is completely degraded by Fe/hv but not by irradiation control. This may probably be due to sharp difference in distribution of chlorine atom in two benzene rings resulting into high polarity of the molecule thus leading to rapid degradation of the compound by the action of photoassisted iron catalyzed reaction.



In order to justify all such anomalies in the concentration of various congeners of dioxins and furans the author should critically review each of the mass spectrum and illustrate the processed data for the benefit of the reader. Had there been some kinetic data of degradation of dioxins and furans the results could be interpreted in a better way.

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