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Photochemical Dechlorination of 2,3,7,8-, 1,3,6,8-, and 1,2,3,4-Tetrachlorodibenzo-*p*-dioxins as Studied by the Frontier-Electron Reactivity Indexes

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The photochemical dechlorination mechanism of 2,3,7,8-, 1,3,6,8- and 1,2,3,4-tetrachlorodibenzo-*p*-dioxins (TCDDs) were theoretically studied by the parametric method 3-modified neglect of diatomic overlap (PM3-MNDO) reactivity indexes based on the frontier electron theory. The theoretical predictions were in good agreement with the experimentally postulated pathways of the photochemical dechlorination of TCDDs.

Keywords environmental dioxins; photochemical dechlorination; PM3-MNDO; frontier electron reactivity index

Introduction

Polychlorodibenzo-*p*-dioxins (PCCDs) are recognized as the highly toxic compounds formed as trace contaminants in the synthetic process of several important commercial products. Photodegradation is a major factor affecting the fate of these environmental chemicals. The solubilities and photochemical reactivities of these chemicals are known to be greatly governed by various materials widespread in aquatic environment systems such as humic substances and natural photosensitizers.[1,2]

In the present work we are concerned in particular with basic relationships between the electronic properties of photoexcited reactive species and the photodegradation pathways of environmental dioxins. To make a preliminary prediction on the photodegradation pathway, the electronic properties of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (TCDD) and its possible photodegradation products were calculated by the simple Huckel molecular orbital (HMO) method.[3] In this case, however, several important points of the experimentally postulated pathway were only partially rationalized by theoretical calculation. The reason for this may be understood in terms of the intrinsic limit of the simple HMO method. That is, this method is not enough appropriate for treatment of the electronic polarization interactions associated with the excited-state configuration playing an important role in the photochemical reactivity.

The aim of this work is to perform a more elaborate theoretical study on the photodegradation pathways of several TCDDs which were recently studied experimentally.[4-6] For this purpose, we shall take advantage of the photochemical reactivity index calculated by the parametric method 3 (PM3) developed as an up-to-data version of the modified neglect of diatomic overlap (MNDO) method.[7] This technique is expected to give reliable results because its chemical accuracy has been much improved by the rigorously refined parametrization for the core Hamiltonian.

Calculation Method

Calculations were performed with the PM3 method contained in the advanced version (Ver. 6.0) of the MOPAC program package.[8] Computations with a greater number of basis orbitals required for large molecules were achieved by enlargement of the array dimensions of the original program.

Initial input geometries of the dioxins were set up as follows. The C–C–O–C dihedral angles of the parent ring were started as 10°, the C–C bond lengths as 1.41 Å, the C–H bond lengths as 1.09 Å, the C–Cl bond lengths as 1.75 Å, and the C–O bond lengths as 1.37 Å. Bond angles were initially assumed to be 120° for the C–C–C, Cl–C–C and H–C–C bonds. The C–O–C bond angles were input as 118.5°. The optimization computation was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method,[9] provided as the option program of MOPAC, where the iteration convergence was attained with the standard criteria of SCF and geometric optimization fully satisfied. The PM3 calculation was performed on the first excited state corresponding to the single-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Both the singlet and triplet states were considered as the spin multiplicity of the first excited state, where the triplet state was calculated by the half-electron method[10,11] provided as the option program of MOPAC. Most of the calculation was performed on a FACOM M-760/8 computer with 24 megabytes of internal memory.

Results and Discussion

The photodegradation of 2,3,7,8-, 1,3,6,8- and 1,2,3,4-TCDDs in dioxane solvent chosen as a model medium for aquatic systems has been recently investigated in detail by the GC/MS analysis of degradation products.[4-6] The major photodegradation pathways were then postulated as the step-by-step dechlorination shown by Fig. 1—3. This indicates that the TCDDs are gradually converted by the photodegradation to less-chlorinated congeners with lower toxicities. Each of the dechlorination steps may be categorized into the photochemical aromatic substitution in proton-releasable solvent such as dioxane.

Prior to the PM3 calculation, the availability of this method to PCDDs was examined in terms of prerequisite correlations between the optimized molecular geometries and the bent structures characteristic of PCDDs. For this purpose, the optimized data on the average value (θ) of the two ether linkage (C–O–C) bond angles, which has been accepted as an appropriate index for monitoring the extent of the bent structure of PCDDs,[12] were compared with the corresponding data estimated from vapor phase Fourier Transform infrared (FTIR) spectra.[13] The optimized θ values of several PCDDs for which FTIR data are available are shown as follows with the corresponding FTIR data in parentheses: 117.4° (116.8°) for 2,7-PCDD, 115.9° (115.1°) for 2,3,7,8-PCDD, 114.9° (114.7°) for 1,2,3,4,8-PCDD, 112.2° (110.0°) for 1,2,3,4,7,8-PCDD and 110.3° (108.5°) for 1,2,3,4,6,7,8-PCDD. The result shows con-

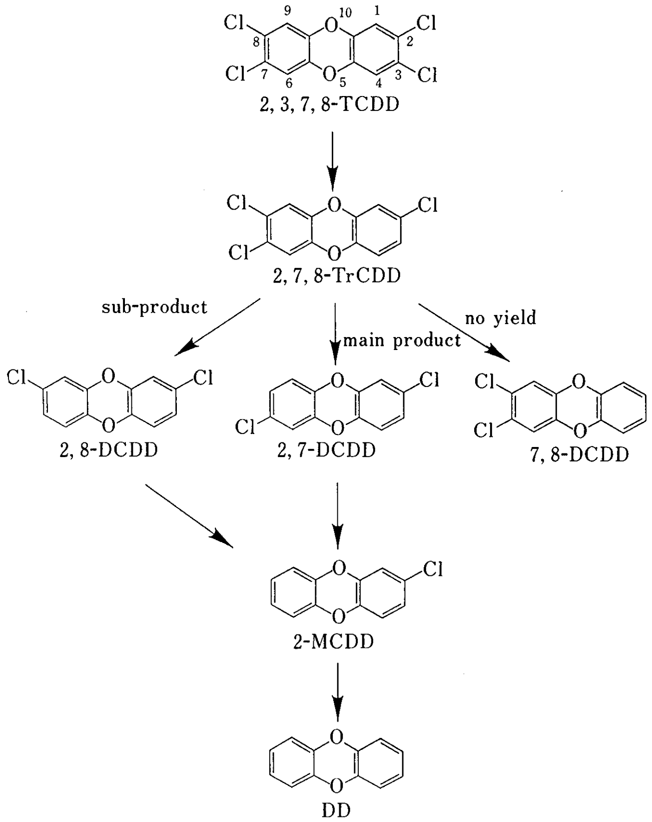

Fig. 1. Experimentally Postulated Pathway of the Photodechlorination of 2,3,7,8-TCDD

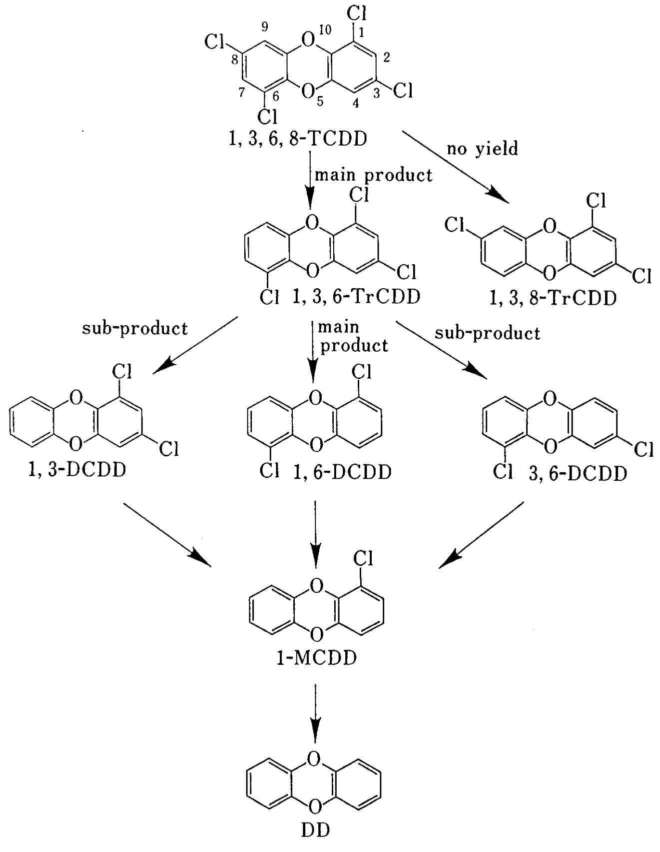

Fig. 2. Experimentally Postulated Pathway of the Photodechlorination of 1,3,6,8-TCDD

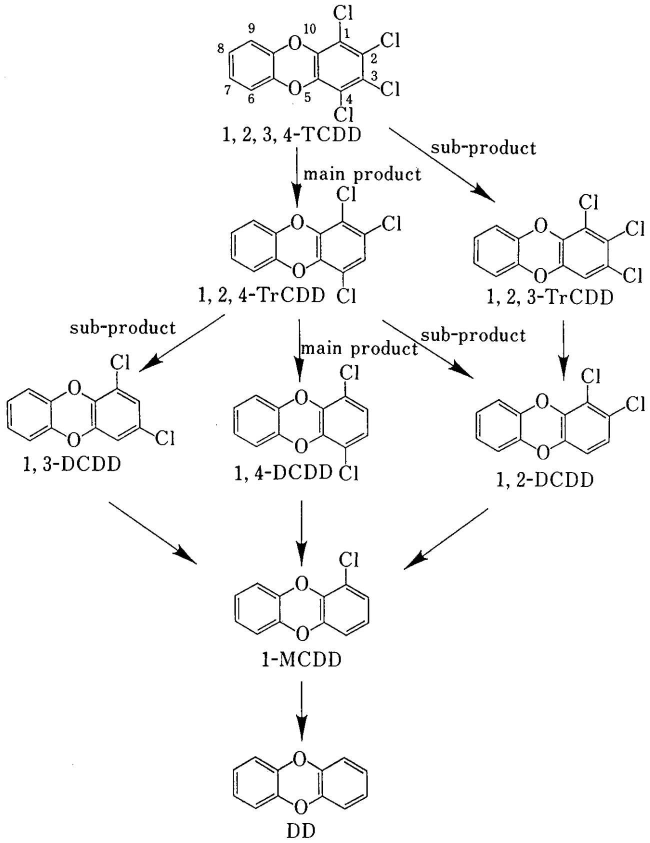

Fig. 3. Experimentally Postulated Pathway of the Photodechlorination of 1,2,3,4-TCDD

siderably good agreement between the optimized and estimated values, although some deviations of about 2° are seen between the two data on hexa- and heptachlorinated PCDDs sterically crowded.

The PM3 calculation may then be regarded as adequate for taking account of the actual effect of chlorine substituents which has been characterized to give near-planar θ values for PCDDs with only lateral (2,3,7,8) chlorines, intermediate θ values for PCDDs with one longitudinal (1,4,6,9) chlorine per aromatic ring and near-tetragonal θ values for PCDDs with two longitudinal chlorines on a single aromatic ring.[12] The analogous effect of chlorine substituents on the optimized θ values was recognized throughout the PCDDs investigated here. The optimized θ values showed a tendency to decrease by 1°—3° upon the first excitation of the PCDDs to both the singlet and triplet spin states. This tendency indicating the decreased planarity of the first excited PCDDs was especially appreciable in the case of the PCDDs asymmetrically substituted by chlorines, possibly due to the increased effect of electronic polarization interactions in the excited state. Summing up the above results, it may be expected that the PM3 method is applicable to the incorporation of the geometrical features or the bent structures of PCDDs which would potentially affect the PCDD electronic properties in the first excited state.

As shown by Figures 1—3, the photochemical dechlorination of 2,3,7,8-, 1,3,6,8- and 1,2,3,4-TCDDs proceeds by the step-by-step aromatic substitutions. The photochemical dechlorination of PCDDs in proton-releasable solvents has been regarded as primarily due to the attack of electron-seeking or positively charged reagents such as the proton released from solvent.[14] It is then natural to assume that the photochemical dechlorination investigated here occurs via the formation of charge-transfer transient complexes in which the highest singly occupied molecular orbital (SOMO*) of the first excited species would act as an electron-donor level to the electrophilic reagents. The photochemical substitution mechanism proposed here is apparently analogous to the electrophilic substitution reaction which has been generally recognized for a number of aromatic molecules.[15] However, the proposed mechanism in which the SOMO* is thought to be important should be discriminated from the aromatic electrophilic substitution which is dominated by the HOMO of the ground state.

According to the proposed substitution mechanism, we shall refer to the photochemical reactivity index based on the frontier electron theory,[16] which claims the important contribution of the frontier electron to stabilization of transient complexes formed in the reaction course. The reactivity index for the photochemical substitution reaction can thus be represented in terms of the frontier spin densities of the SOMO* behaving as an electron-donor level to the electron-seeking reagents. This index was calculated for both the singlet and triplet spin states of the first excited species. In what follows, the index values of the singlet and triplet states will be referred to as $f_R^*(S)$ and $f_R^*(T)$, respectively.

In Tables I—III are collected the $f_R^*(S)$ and $f_R^*(T)$ indexes calculated for the substitution centers of 2,3,7,8-, 1,3,6,8- and 1,2,3,4-TCDDs and their photodechlorination products. Prior to further investigations, it should be mentioned that the $f_R^*(S)$ and $f_R^*(T)$ indexes exhibit several distinctions from the LUMO spin densities (f_{LUMO}) of the corresponding ground state. Part of this may be understood in terms of the difference in the extent of the bent structures associated with the ground and first excited PCDDs. That is, the marked difference such as seen between the lateral and longitudinal $f_R^*(S)$ and $f_R^*(T)$ indexes was not reflected in the f_{LUMO} values, although the f_{LUMO} values at the lateral positions were always larger than those at the longitudinal positions. Moreover, for the PCDDs having two and more lateral chlorines, the relative magnitudes of the $f_R^*(S)$ and/or the $f_R^*(T)$ indexes of the different lateral positions, which are important in predicting the photodechlorination pathway, were frequently

TABLE I. Photoreactivity Indexes of 2,3,7,8-TCDD and Its Photodechlorination Products

Reaction site	2,3,7,8-TCDD	2,7,8-TrCDD	2,7-DCDD	2,8-DCDD	7,8-DCDD	2-MCDD
1	0.0091 (0.0095)	0.0041 (0.0034)	0.0035 (0.0031)	0.0032 (0.0027)	0.0068 (0.0062)	0.0036 (0.0032)
2	0.0823 (0.0816)	0.0728 (0.0738)	0.0872 (0.0879)	0.0889 (0.0898)	0.0605 (0.0594)	0.0927 (0.0934)
3	0.0823 (0.0816)	0.0682 (0.0685)	0.0840 (0.0844)	0.0831 (0.0823)	0.0605 (0.0594)	0.0892 (0.0889)
4	0.0091 (0.0095)	0.0054 (0.0057)	0.0051 (0.0047)	0.0056 (0.0053)	0.0068 (0.0062)	0.0054 (0.0052)
6	0.0091 (0.0095)	0.0101 (0.0103)	0.0035 (0.0031)	0.0056 (0.0053)	0.0035 (0.0033)	0.0069 (0.0065)
7	0.0823 (0.0816)	0.0949 (0.0931)	0.0872 (0.0879)	0.0831 (0.0823)	0.0998 (0.1019)	0.0672 (0.0669)
8	0.0823 (0.0816)	0.0932 (0.0957)	0.0840 (0.0844)	0.0889 (0.0898)	0.0998 (0.1019)	0.0688 (0.0699)
9	0.0091 (0.0095)	0.0029 (0.0023)	0.0051 (0.0047)	0.0032 (0.0027)	0.0035 (0.0033)	0.0064 (0.0052)

$f_R^*(T)$ is given in parenthesis under $f_R^*(S)$.

TABLE II. Photoreactivity Indexes of 1,3,6,8-TCDD and Its Photodechlorination Products

Reaction site	1,3,6,8-TCDD	1,3,6-TrCDD	1,3,8-TrCDD	1,6-DCDD	1,3-DCDD	3,6-DCDD	1-MCDD
1	0.0062 (0.0068)	0.0050 (0.0054)	0.0074 (0.0070)	0.0054 (0.0052)	0.0062 (0.0074)	0.0068 (0.0072)	0.0081 (0.0077)
2	0.0740 (0.0735)	0.0714 (0.0703)	0.0752 (0.0779)	0.0771 (0.0767)	0.0832 (0.0850)	0.0754 (0.0769)	0.0761 (0.0765)
3	0.0858 (0.0863)	0.0643 (0.0638)	0.0913 (0.0927)	0.0819 (0.0827)	0.1045 (0.1029)	0.0913 (0.0926)	0.0863 (0.0888)
4	0.0037 (0.0032)	0.0079 (0.0074)	0.0022 (0.0029)	0.0062 (0.0057)	0.0028 (0.0026)	0.0039 (0.0038)	0.0045 (0.0047)
6	0.0062 (0.0068)	0.0026 (0.0030)	0.0050 (0.0054)	0.0054 (0.0052)	0.0053 (0.0057)	0.0055 (0.0051)	0.0069 (0.0061)
7	0.0740 (0.0735)	0.0971 (0.0977)	0.0769 (0.0752)	0.0771 (0.0767)	0.0657 (0.0661)	0.0768 (0.0752)	0.0735 (0.0730)
8	0.0858 (0.0863)	0.0822 (0.0817)	0.0762 (0.0760)	0.0819 (0.0827)	0.0643 (0.0633)	0.0689 (0.0692)	0.0720 (0.0719)
9	0.0037 (0.0032)	0.0072 (0.0074)	0.0035 (0.0041)	0.0062 (0.0057)	0.0069 (0.0061)	0.0061 (0.0059)	0.0068 (0.0062)

$f_R^*(T)$ is given in parenthesis under $f_R^*(S)$.

TABLE III. Photoreactivity Indexes of 1,2,3,4-TCDD and Its Photodechlorination Products

Reaction site	1,2,3,4-TCDD	1,2,4-TrCDD	1,2,3-TrCDD	1,4-DCDD	1,2-DCDD
1	0.0042 (0.0036)	0.0043 (0.0040)	0.0048 (0.0044)	0.0066 (0.0065)	0.0049 (0.0046)
2	0.1067 (0.1085)	0.1009 (0.1001)	0.1059 (0.1007)	0.0843 (0.0857)	0.0892 (0.0902)
3	0.1067 (0.1085)	0.0932 (0.0941)	0.1088 (0.1124)	0.0843 (0.0857)	0.0925 (0.0910)
4	0.0042 (0.0036)	0.0059 (0.0063)	0.0021 (0.0025)	0.0066 (0.0065)	0.0042 (0.0048)
6	0.0048 (0.0057)	0.0062 (0.0063)	0.0064 (0.0059)	0.0060 (0.0062)	0.0071 (0.0068)
7	0.0563 (0.0545)	0.0608 (0.0606)	0.0557 (0.0569)	0.0699 (0.0680)	0.0639 (0.0636)
8	0.0563 (0.0545)	0.0617 (0.0615)	0.0562 (0.0569)	0.0699 (0.0680)	0.0654 (0.0667)
9	0.0048 (0.0057)	0.0045 (0.0058)	0.0050 (0.0055)	0.0060 (0.0062)	0.0067 (0.0054)

$f_R^*(T)$ is given in parenthesis under $f_R^*(S)$. The indexes of 1,3-DCDD and 1-MCDD yielded from 1,2,3,4-TCDD are given in Table II.

in poor agreement with the relative magnitudes of the corresponding f_{LUMO} values. From the photochemical reactivity indexes given in Tables I—III, we can note the following.

For all of the TCDDs, both the $f_R^*(S)$ and $f_R^*(T)$ indexes of the lateral (2,3,7,8-) positions are much higher than those of the longitudinal (1,4,6,9-) positions. This correctly predicts that the photodegradation of the TCDDs is initiated by dechlorination at the lateral positions, although it is difficult to discern the relative contributions of the singlet and triplet excited species to this reaction.

For 2,7,8-, 1,3,6-, 1,2,4- and 1,2,3-trichlorinated dibenzo-*p*-dioxin (TrCDD) actually yielded by the first photodechlorination step, the $f_R^*(S)$ ($f_R^*(T)$) indexes are in the order of $2<8<7$ ($2<7<8$), $6<1<<3$ ($6<1<<3$), $1<4<<2$ ($1<4<<2$) and $1<<2<3$ ($1<<2<3$), respectively.

With respect to 1,3,6-, 1,2,4- and 1,2,3-TrCDDs, both the $f_R^*(S)$ and $f_R^*(T)$ indexes are in good correlation with the experimentally postulated pathways. That is, 1,3,6-TrCDD yields as main product 1,6-dechlorinated dibenzo-*p*-dioxin (DCDD) and as subproducts 1,3- and 3,6-DCDDs. 1,2,4-TrCDD yields as main product 1,4-DCDD and as subproducts 1,2- and 1,3 DCDDs. 1,2,3-TrCDD yields only 1,2-DCDD. With respect to the photodechlorination pathway of 2,7,8-TrCDD, the $f_R^*(T)$ index gives a correct prediction, while such is not the case for the $f_R^*(S)$ index. That is, 2,7,8-TrCDD yields as main product 2,7-DCDD, as subproduct 2,8-DCDD, but does not yield 7,8-DCDD. For reference, the f_{LUMO} value of 2,7,8-TrCDD in the ground state is also in the same order as found for the $f_R^*(S)$ index. This implies that the correct predictability of the $f_R^*(T)$ index may be related to the spin population characteristic in the triplet state under consideration.

For DCDDs and MCDDs to be yielded in the second and third photodechlorination steps, respectively, the $f_R^*(S)$ and $f_R^*(T)$ indexes are still much higher at the lateral sites than at the longitudinal sites, although there are some differences between the magnitudes of the two indexes for each congener. This is again in accord with the experimentally postulated pathways of the photodechlorination of these congeners.

The present work indicates that the photodechlorination pathways of 2,3,7,8-, 1,3,6,8- and 1,2,3,4-TCDDs are well explainable by the photochemical reactivity indexes based on the frontier electron theory, although it is difficult to give a definite identification of the relative contributions of the singlet and triplet excited species. The main reason may be the superior chemical concept of the frontier electron theory itself. Another important reason may be that the PM3 method developed to extend the availability of the original MNDO approximation is enough adequate for treating the electronic polarization interactions such as are associated with the excited-state configuration.

The utility of this method is essentially supported by its predictive capability with respect to a fundamental trend: the photochemical dechlorination of PCDDs occurs preferably at the lateral positions rather than at the longitudinal positions and, in particular, at the adjacent lateral positions rather than at the non-adjacent lateral positions. An analogous trend has been widely observed in the photodegradation of halogenated dibenzo-*p*-dioxins in various media modeling aquatic and/or lipophilic environmental compartments.[17—24] This strongly suggests that the quantum chemical approach such as was attempted in this work is a useful method of predicting and/or understanding the major photodegradation pathways of environmental dioxins on the basis of the electronic properties of the photoexcited reactive species.

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