

Reactions of Diphenyl Ether with Chlorine and Bromine Atoms Around 750 K – Relevance for Gas-Phase “Dioxin” Formation

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The title reactions have been studied to scrutinize rate data recently inferred for the two reverse steps – reaction of phenoxy radicals with chlorobenzene and bromobenzene – which were at variance with commonly accepted model values. Both with chlorine and bromine atoms, splitting to halobenzene and phenoxy radical was found to occur in competition with abstraction of *o*-, *m*-, *p*-hydrogen atoms. On

this basis, the displacements of Cl and Br from the benzene ring by phenoxy radicals must have activation energies above 20 kcal/mol, and are therefore slow. As a consequence, formation of “dioxins” from halogenated phenols, in (slow) combustion, should proceed by combination of two (halo)phenoxy radicals rather than by displacement of (*ortho*-)halogen in a halophenol molecule.

Introduction

The origin and formation mechanisms of polychlorinated dibenzo-*p*-dioxins and furans (“dioxins”, PCDD/F) continue to be heavily debated and researched. Their demonstrated high toxicity especially to some test animals has led to stringent regulations in parts of Europe, the USA, and in Japan. Meanwhile, the real dioxin deposition is much bigger than the estimated total emission from known sources^[1] and the major pathways in dioxin formation are still ill-defined.

Combustion processes, especially those of Municipal Solid Waste, are an important source of PCDD/F.^[2] Since it became known that the levels of PCDD/F increased considerably upon the passage of the primary combustion gases through Air Pollution Control devices (ESP, baghouse)^[3] much research effort has been devoted to unravel pertinent mechanisms. Two distinct pathways have been proposed: (i) So-called “de novo” synthesis from carbonaceous materials on solid surfaces (ashes) in a sequence of steps catalyzed by metals, on a long time scale (up to hours).^[2,4,5] (ii) Formation from “precursors”, primarily (chloro)phenols. Model experiments have shown that ashes can create especially PCDD efficiently in the temperature region of 300–400 °C within seconds.^[5] However, little PCDF is found, meaning that this precursor scenario is too simple. Other precursors may play a part, too.

The gas-phase formation has already been discussed by Shaub and Tsang (S&T) in 1983^[6] with trichlorophenol as an example; a model mechanism involving 13 gas-phase (radical) reactions was proposed. Displacement of an *ortho*-chlorine in the (chloro)phenol P by a (trichloro)phenoxy radical P[•] (Reaction 1) was advanced as a key step, leading to the corresponding *ortho*-hydroxydiphenyl ether (PD in

S&T's notation). PD was believed to react rapidly to a (chlorinated) dioxin D by loss of HCl (Reaction 2).



Step 1, with an estimated activation energy of 26 kcal/mol, should give perceptible rates only at higher temperatures, but then the phenoxy radicals will decompose.^[7] As a result, the “S&T” gas-phase model can only account for low dioxin levels throughout.

Since in practice dioxin emissions exceed the levels predicted by S&T, the process was reinvestigated by Sidhu and co-workers.^[8] They studied the thermal decomposition of 2,4,6-trichloro- and 2,4,6-tribromophenol in excess of air in a flow reactor. The experiments were done over a temperature range of 300–800 °C with minimal contribution of surface reactions. Maximum yields of PCDD were obtained around 600 °C. In order to adjust the “S&T” model to those observations they decreased the activation energy of Reaction 1 to 19.5 kcal/mol for chlorinated phenols, and to 8.8 kcal/mol for the corresponding brominated case (to account for a factor 500 higher value). On this basis they suggested that gas-phase formation – by the S&T mechanism – could make a significant contribution to the observed PCDD/F yields in full-scale incinerators.

Both studies ignored an alternative, viz. condensation by combination of two (chloro)phenoxy radicals. It has been known for a long time that thermal conversions of phenol lead to dibenzofuran, and closer investigations have shown that this involves the combination of two (unchlorinated) phenoxy radicals with an overall rate constant of 10⁸ M⁻¹s⁻¹ or higher.^[9,10] Chlorinated phenols still containing a hydrogen atom in *ortho* position react analogously. In “mixed” situations, with both H and Cl present in *ortho* position, as in *o*-Cl-phenol, the appropriate DCDFs are formed, but also (Cl-free) dibenzodioxin, the “S&T”-like product.^[9] Whatever the details of the respective pathways, it is reasonable to accept radical/radical combination as a key step in both types of reaction, formation of dibenzofu-

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ran – with formal loss of the elements of water – and of dibenzodioxin, with net overall loss of two chlorine atoms.



Returning to the example of 2,4,6-TCP^[8] it will be clear that the result of a competition between Reactions 1 and 3 as key steps – with greatly different rate constants – is governed by the (actual) $P^{\bullet}/P$ ratio. Depending on the temperature, for Reaction 1 to “win”, the concentration of (chloro)phenol should be at least some five powers of ten larger than that of the chlorophenoxy radical. Useful (experimental) data on this are lacking, however.

In order to check the kinetics of the S&T model, Louw and Grotheer^[11] have recently investigated the co-combustion of phenol and chlorobenzene, to obtain rate parameters for Reaction 4, the simplest analogue of Reaction 1.



The direct reaction product, diphenyl ether (PhOPh), is more stable than phenolic compounds like PD, and can be easily determined. Moreover, the products from Reaction 4 can be distinguished from those of Reaction 3. Since unchlorinated phenol was used as a source of phenoxy radicals the only one “dioxin” product was dibenzofuran (Reaction 5).



Later on the study had been extended to bromobenzene.^[12] Since HBr, produced from the slow combustion of PhBr, can affect the overall rate coefficient of the DF formation from phenoxy radicals the competition between chloro- and bromobenzene was investigated as well. Remarkably Reaction 6 with PhBr was not much faster than Reaction 4 with PhCl. The activation energy of Reaction 4 was derived to be 24.5 kcal/mol (corresponding well with E_a estimated in the S&T model). For Reaction 6 E_a was found to be 21.4 kcal/mol, much higher than the 8.8 kcal/mol proposed by Sidhu and co-workers^[8] to comply with the “S&T” model. This let Grotheer and Louw conclude that in both studies Reaction 1 was insignificant compared to Reaction 3 in the gas-phase formation of dioxin.

The energy diagrams (Figures 1 and 2) are helpful in a further analysis of the possible importance of the parent Reactions 4 and 6 of the S&T model.

For the reaction of PhOPh with $\text{Cl}^{\bullet}$ or $\text{Br}^{\bullet}$ there are two possibilities: (i) splitting, by *ipso* addition, to phenoxy radicals and chlorobenzene (Reaction –4) or bromobenzene (Reaction –6); (ii) formation of halogenated phenoxybenzenes, by H abstraction.

If the data of Sidhu et al. apply, chlorine atoms would split the ether rather than abstract hydrogen; bromine atoms and PhOPh should give bromobenzene and phenoxy radicals exclusively, with no chance for hydrogen abstraction. With the data of Grotheer and Louw, however, $\text{Cl}^{\bullet}$ can follow both pathways (i) and (ii). With $\text{Br}^{\bullet}$ the endo-

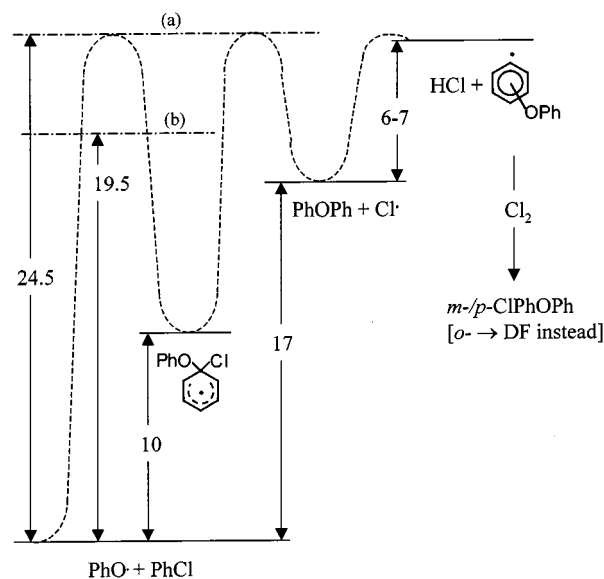


Figure 1. Enthalpy diagram for Reaction 4 and related processes (energy data in kcal/mol); TS (a) according to ref.^{[11][12]}; TS level (b): modeled value of Sidhu et al.^[8] for 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{O}(\text{H})$

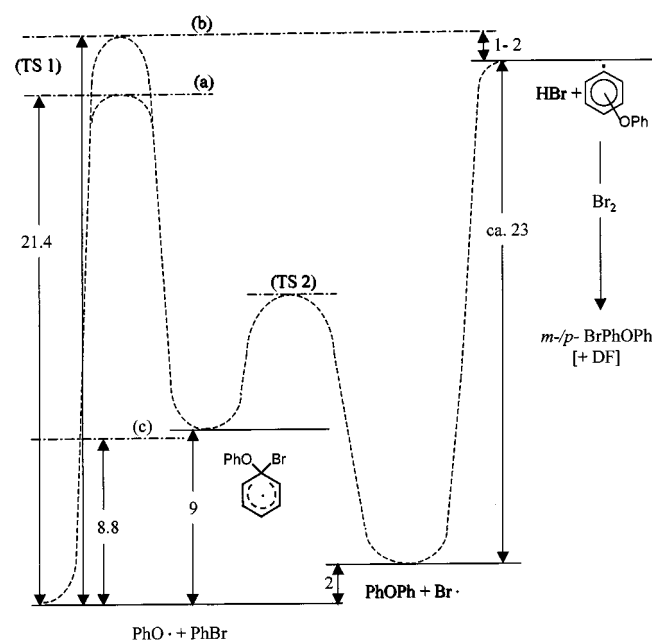


Figure 2. Enthalpy diagram for Reaction 6 and related processes (energy data in kcal/mol); TS (a) according to ref.^[12]; TS (b) this work; TS level (c): modeled value of Sidhu et al.^[8] for 2,4,6- $\text{Br}_3\text{C}_6\text{H}_2\text{O}(\text{H})$

thermicity of the H abstraction together with the 21.4 kcal/mol barrier for Reaction 6 would again suggest pathways (i) and (ii) to be competitive.

The gas-phase chlorination of benzene derivatives (ArH) has been studied by Kooyman and co-workers.^[13] This thermal process proceeds by H abstraction, $\text{Cl}^{\bullet} + \text{ArH} \rightarrow \text{HCl} + \text{Ar}^{\bullet}$ as key step, the latter species giving ArCl by reaction with Cl_2 (or another appropriate Cl donor).^[14] With PhOPh the reported main products are *m*- and *p*- $\text{ClC}_6\text{H}_4\text{OPh}$ and dibenzofuran^[15] (the *o*-phenoxyphenyl radical cyclizes in-

stead of giving *o*-ClC₆H₄OPh). Formation of chlorobenzene, if any, was not mentioned. Gas-phase bromination is known to follow the same mechanism,^[13] but in this case diphenyl ether has not been reported on.

In order to obtain a better insight we have re-investigated the gas-phase chlorination of PhOPh with emphasis on the possible importance of Reaction –4. In order to prove or disprove the overall high barrier for Reaction 6 – depicted as TS1 in Figure 2 for reasons to follow – the gas-phase reaction of PhOPh with bromine has also been studied. For proper comparison, conditions (temperature, dwell times, concentrations of arenes) have been designed close to those of the “forward” slow combustion.^[11,12] The desired temperatures are quite high for halogenation, however; reactions involving Br₂ proceeded well at 500°C, but Cl₂ then is too aggressive; in the latter case C₂Cl₆, smoothly generating Cl atoms^[14] has been employed.

Results and Discussion

(i) Chlorination

With hexachloroethane as a source of chlorine atoms and tetrachloromethane as chlorine donor to reactive (aryl) radicals if formed, a series of runs have been conducted at temperatures of 460–480°C. At 500°C the product contained quite a lot of sooty material – in accordance with earlier observations on this chlorination agent.^[14] Key data are collected in Table 1.

The formation of C₂Cl₄ (ca. 10% on C₂Cl₆ at 460°C, ca. 20% at 480°C) shows that (atomic) chlorine is generated; the identification of *m*- and *p*-ClC₆H₄OPh together with comparable amounts of dibenzofuran demonstrates that (overall) chlorination by H-abstraction does occur. Our product ratios *m*-/*p*- = 4–5, and [DF] ≈ [*m*- + *p*-], resemble those of Engelsma^[15] for gas-phase chlorination with Cl₂ in the same temperature range. Interestingly, the formation of chlorobenzene, at substantial levels (about one-half of DF) shows that on a per-site basis, splitting of PhOPh by Cl•, Reaction –4, is as fast as H abstraction. At this point it is important to note that PhOPh itself is thermally very stable. The Arrhenius parameters for bond fission to phenyl and phenoxy radicals (log *A* = 15.5 M⁻¹s⁻¹; *E*_a = 75 kcal/mol^[16]) entail *k* ≤ 10⁻⁶ s⁻¹ at the temperatures used. Blank

runs of PhOPh/PhCN indeed gave negligible outputs of DF and of course no chlorobenzene.

At lower to trace levels, a large number of other products are also formed. These include typical products from the perchloro C₁/C₂ mix, e.g. hexachlorobutadiene, hexachloropropene, and hexachlorobenzene. Trichloromethylbenzene illustrates the intermediacy of CCl₃ radicals. The most likely explanation for formation of this compound is *ipso*-substitution of PhOPh to give PhO• and PhCCl₃. Another example of *ipso*-substitution is the observation of two isomers of PhOC₆H₄Ph, with abundance of about 5% on those of *m*- and *p*-ClC₆H₄OPh. It is very likely that the corresponding *m*-(*p*)-PhOC₆H₄ radicals will have reacted with PhOPh, with *ipso* displacement of PhO as the productive channel. Note that with CCl₄/C₂Cl₆ as chlorination agent for benzene derivatives ArH, part of the aryl radicals Ar• generated will react with ArH to create biaryls Ar–Ar.^[14] With PhOPh the corresponding products, isomers of PhOC₆H₄-C₆H₄OPh were too involatile to be seen in our GC analysis. The *ipso* product PhOC₆H₄Ph is a proper manifestation of this type of reaction.

Splitting (Reaction –4) implies formation of phenoxy radicals next to chlorobenzene. Their fate is not yet sure. The formation of phenol by recombination of PhO• and H• radicals is fast (*k* = 2·10¹¹ M⁻¹s⁻¹^[17]), but the concentration of atomic hydrogen will be extremely low. In fact no phenol could be detected, showing that other pathways for acquiring hydrogen are negligible as well.

Condensation of two phenoxy radicals (Reaction 5) leads to DF, the same product as that from *o*-PhOC₆H₄• cyclization. PhO• can also become chlorinated before condensation.^[18] At least two isomers of DCDF were produced, but at a very low level (less than 1% on DF, each). MCDF was not seen at all. One of the products with low abundance was identified by the MS search library as 2-chlorobenzoyl chloride. Without detailing possible mechanistic pathways, we suggest this to be a product stemming from reaction between phenoxy and CCl₃ radicals.

In sum, the exact fate of PhO• is not known; but should DF have been formed with a high efficiency, the maximum contribution via PhO• + PhO• combination would be 0.5 that of PhCl, or ca. 25% of the DF output.

The output of HCl is several times larger than the amount of Cl which must have become free in the formation

Table 1. Chlorination/chlorinolysis of diphenyl ether^[a]

Exp. no.	Temp. [°C]	Inflow ^[b]		Outflow ^[c]					HCl
		C ₂ Cl ₆	PhCN	C ₂ Cl ₆	C ₂ Cl ₄	PhCl	DF	<i>m</i> -/ <i>p</i> -ClC ₆ H ₄ OPh	
C1	460	4.05	10.1	3.80	0.36	0.062	0.15	0.23/0.047	1.56
C2	460	3.00	–	2.82	0.28	0.067	0.16	0.27/0.066	1.40
C3	480	4.05	10.1	3.13	0.84	0.47	0.89	0.69/0.18	5.8
C4	480	4.05	10.1	3.42	0.87	0.48	0.93	0.72/0.19	6.5
C5	480	4.05	10.1	3.01	0.77	0.50	0.86	0.62/0.16	6.7
C6	480	3.00	–	2.55	0.75	0.53	0.97	0.73/0.19	4.6
C7	480	3.00	–	2.59	0.68	0.44	0.83	0.68/0.18	4.4

^[a] Run times: 60 min (exp. C1, C3–C5) or 85 min (C2, C6, C7); residence time 150 ± 2 s; flow data in mmol/h. – ^[b] Other inflows: N₂ = 270; PhOPh = 20.1; CCl₄ = 20.2 mmol/h. – ^[c] Recoveries of PhOPh 75–92%; PhCN > 95%; CCl₄ > 80%.

Table 2. Bromination/brominolysis of diphenyl ether at 500°C^[a]

Exp. no.	PhOPh	Inflow Diluent ^[b]	Br ₂	PhBr	DF	Outflow <i>m</i> -/ <i>p</i> -BrC ₆ H ₄ OPh	HBr
B1	24.7	17.4	4.6	0.27	1.59	0.82/0.68	6.6
B2	24.7	17.4	4.7	0.32	1.70	0.95/0.82	6.6
B3	24.7	17.4	4.5	0.31	1.63	0.93/0.80	6.5
B4	32.1	4.6	4.6	0.40	2.27	1.51/0.50	6.5
B5	32.1	4.6	4.6	0.45	2.39	1.62/0.53	6.8
B6	16.05	2.3	2.3	0.17	0.94	0.56/0.27	3.6

^[a] Residence time 153±2 s; flows in mmol/h. — ^[b] In exp. B1–B3 benzonitrile was used, in exp. B4–B6 *p*-difluorobenzene.

of C₂Cl₄. This merely shows that CCl₄ is also contributing to “mineral” chlorine. Likewise the amount of hydrogen in HCl is larger than that removed, displaced, in the phenyl ether products of Table 1. Unspecified condensation reactions (usual in pyrolytic reactions) must be responsible for this.

In experiments C1 and C3–C5 benzonitrile was co-fed with PhOPh. In those runs the three isomers of ClC₆H₄CN were produced; the ClC₆H₄CN output indicated that PhCN was 5 times less reactive than PhOPh – in accordance with earlier observation.^[13]

As can be seen from the ratios of DF/*m*-/*p*-ClC₆H₄OPh (Table 1), PhCN has no influence on the investigated reactions.

(ii) Bromination

PhOPh was admixed with benzonitrile or *p*-difluorobenzene, and Br₂ served as the source of Br atoms. Additional experiments were done to check whether benzonitrile can react with bromine under the prevailing conditions to give bromobenzene. No PhBr was found. PhOPh was 4–5 times more reactive than PhCN. The pattern of isomeric bromobenzonitriles was similar to that reported in the literature.^[15] In exp. B1–B3 the *o*/*m*/*p* ratio of BrC₆H₄CN was 18:49:33 compared with 23:49:28 at the same temperature.^[15]

As can be seen in Table 2, the *m*-/*p*- ratios of BrC₆H₄OPh are smaller than in the case of chlorination, but still the main organic product was DF, and as in the chlorination yields of DF are about equal to the sum of *m*- and *p*-BrC₆H₄OPh. The reason for such small *m*-/*p*- ratios (1.2 and 3 for the mix with PhCN and C₆H₄F₂, respectively) may be that some residual Br₂ causes electrophilic “after”-bromination, which will involve the *p*-position only. Furthermore, if the conversion of Br₂ nears completion, the HBr/Br₂ ratio becomes high. Then *m*- and *p*-PhOC₆H₄ radicals will also react with HBr, regenerating PhOPh. Such possible influences on the output of *m*- and *p*-BrC₆H₄OPh are much smaller, if present at all, in case of the *o*-PhOC₆H₄ radical, which unimolecularly reacts to DF.

As has been already discussed in the chlorination case, some of the DF may have been produced from PhO•. In the bromination case the maximal DF yield from 2 PhO• (0.5 times that of PhBr) comprises only 10% of the total

output. Altogether, the safest way to discuss the competition between ether splitting by halogen atoms and H abstraction is to take one “isomer”: *ortho*, with its straightforward cyclization to DF. The average ratio of PhBr/DF is 0.18, per site it is 0.36 (these values can be up to 10% larger when the production of DF from PhO• is substantial).

So, splitting of PhOPh by Br• is nearly by a factor of 2 slower than hydrogen abstraction from the *ortho*-position.

(iii) Mechanistic Aspects

The per-site rate difference for splitting and abstraction of *ortho*-H by Br• mentioned above implies that, at 500°C, the free enthalpy of activation for splitting is – at most – 1.6 kcal/mol higher than that for abstraction. Possible entropy differences between the two rate-determining steps may make Δ*E*_a somewhat different, but inspection of Figure 2 shows that our result is close to that of Grotheer and Louw for the forward Reaction 6, substantiating that the (overall) barrier for displacement of Br from PhBr by PhO• is well over 20 kcal/mol. In no way would Sidhu’s value, proposed to cover rates of “dioxin” formation from 2,4,6-tribromophenol/phenoxy apply here: Bromine atoms should then have reacted with PhOPh exclusively by splitting – and with a much higher rate than for H abstraction (thence, substitution to ArBr), which should also have left benzonitrile untouched in the PhOPh/PhCN competition.

Bond strengths can, will, depend on structure and on (degrees of) substitution; but differences in bond strengths between R–X and R–Y vary relatively little, certainly if X and Y are of like polar character, as in the case for electronegative groups Br, Cl, and OR. So Figure 2 will expectedly not change much when applied to the case of tribromophenoxy/phenol, and the (higher than expected) rate for “dioxin” formation^[8] must have been due to the (faster) ArO• + ArO• combinations.

In Figure 2, TS2 represents the (exothermal) loss of Br• from the *ipso*-adduct radical. Its level will be far below that of TS1. Being kinetically insignificant for the forward Reaction 6, it merely means that *ipso* addition of Br• to PhOPh is highly reversible. Note that the analogous barrier in the Cl case (Figure 1), for endothermal loss of Cl• from the adduct species vice versa, will approach that for PhO• addition to PhCl. (Both activation barriers have arbitrarily been sketched at the same level.) As a consequence, *ipso*

addition of $\text{Cl}^\bullet$ to PhOPh is expected to be reversible to a limited extent only.

Anyway, in the chlorine case our observed product ratios PhCl/DF – as discussed in section (i) – entail nearly equal rates (activation barriers) for splitting and H abstraction. This is in full accord with the observed E_a for the forward Reaction 4 as reported by Grotheer and Louw.^[11] Should Sidhu's value of 19.5 kcal/mol inferred from the slow combustion of 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{OH}$ apply here, splitting would have been by far the major process. In our view, $\text{ArO}^\bullet + \text{ArO}^\bullet$ combination, etc. must have been at least as important as the S&T-type $\text{ArO}^\bullet + \text{chloroarene}$ displacements. As mentioned above for the bromine case, bond strengths may vary, but the overall endothermicity for the latter type of reaction (17 kcal/mol for our base case $\text{PhO}^\bullet + \text{PhCl}$) should not change drastically upon introducing (chlorine) substituents – let alone that displacement becomes about thermoneutral, or even exothermal, as advanced by Bozzeli et al.^[19] To the best of our knowledge there are no known experimental data to support such a proposal.

Our results on the PhCl(Br) + $\text{PhO}^\bullet$ systems, and vice versa, imply that $\text{PhO}^\bullet$ has only a low reactivity in addition to benzene derivatives, even in the nearly neutral displacement of Br. The reasons for that are not yet clear, but we wish to point out that – while phenoxy-type radicals are of key importance in antioxidant action – next to $\text{ArO}^\bullet$ (self or cross) radical combinations, and “surprisingly fast” $\text{ArO}^\bullet + \text{Ar}'\text{OH} \rightarrow \text{ArOH} + \text{Ar}'\text{O}^\bullet$ hydrogen transfers,^[20] we are unaware of other examples of $\text{ArO}^\bullet + \text{molecule}$ reactions, such as with C=C double bonds.

Experimental Section

All experiments were conducted in a cylindrical, stirred-tanktype flow reactor of 680 ml volume placed in an electrically heated oven. The temperature was controlled by a proportional regulator and monitored with chromel-alumel thermocouples displayed on digital thermometers (Therma 1, type ST-861–107). The upper and lower ends of the oven were insulated by quartz wool. For further details on this type of setup see ref.^[12] Gas flows were regulated by needle valves and measured with capillary flow meters. Liquid (organic) reactants were introduced by means of a calibrated motorized syringe pump (B. Braun, Melsungen, Perfusor VI type 871222/0) via a gas-tight rubber septum and vaporized into the gas flow before entering the reactor. The entrance and exit tubes of the reactor were heated by wrapped heating tape to prevent condensation of the less volatile organics. Condensable products were collected in two cold traps. The first one contained aqueous potassium hydroxide and toluene, and was cooled with ice. The second trap, with toluene, was cooled by acetone with liquid nitrogen. For experiments C1–C7 bromobenzene was used as an external standard and for B1–B6 chlorobenzene. Aromatic compounds were quantified with a Hewlett Packard 5890A gas chromatograph with FID using a CP-SIL5-CB column (50 m $\times$ 0.32 mm ID). 1- μL portions of

liquid samples were injected at a split ratio of 1:15. Absolute concentrations were deduced from the peak areas, after calibration by injecting standard mixtures of known composition. A Hewlett Packard 5890 GC-MS was used to identify unknown products. Outflows of HCl or HBr were quantified by means of a Mettler DL25 automatic titrator. Exit non-condensable gases were analysed using a Packard series 428 GC equipped with FID detector, Carboplot 007 column and a methanizer, calibrated by independent injections of a standard gas mixture. The reaction of chlorine (atoms) was studied at 460–480°C by using diphenyl ether admixed with tetrachloromethane and hexachloroethane^[14] and residence times of about 2 min. Experiments involving bromine atoms were carried out at 500°C, with comparable residence times. Br_2 was fed in from an impinger by a calibrated flow of nitrogen. Here PhOPh was diluted with benzonitrile or *p*-difluorobenzene, both less reactive in gas-phase halogenation than diphenyl ether.^[13,14]

Purity of Reagents: Tank N_2 99.99% was supplied by Hoekloos in a standard cylinder. Diphenyl ether (Merck, pro synthesis), tetrachloromethane (J. T. Baker, > 99%), hexachloroethane (Fluka, pure), benzonitrile (Merck, pro synthesis), *p*-difluorobenzene (Fluka, pure) were checked by GC to be of adequate (> 99%) purity and used as such. Reference compounds such as chlorobenzene, bromobenzene, and dibenzofuran were high-grade (> 99.9) commercial products.

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