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Influence of TiO₂ Surface on 1,2-Chlorine Shift in β -Chlorine Substituted Radicals As **Studied by Radiation Chemistry and Photocatalysis**

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The influence of surface-specific parameters on the photocatalytically induced oxidative degradation of halogenated hydrocarbons in aqueous TiO₂ suspensions has been evaluated by comparing the results obtained in this heterogeneous system with those from γ -irradiated homogeneous aqueous solutions. A 1,2-chlorine shift known to occur in β -chlorinated alkyl radicals and the products obtained upon degradation of these radicals (particularly various chloroacetic acids) have been used as markers in these investigations. The results indicated that this chlorine shift, e.g., the rearrangement of $CCl_3-CH_2^{\bullet} \rightarrow CCl_2-CH_2Cl_1$ occurs much slower (k in the order of 10^6 s⁻¹) at the TiO₂ surface than in the homogeneous solution, where the present data confirm earlier rate constants of $\ge 10^8$ s⁻¹. This slowdown of the rearrangement process is attributed to steric hindrance in the surface-adsorbed state of the radicals. In the heterogeneous systems the rearrangement can, in fact, be interfered with by peroxidation of the unrearranged radical in the presence of molecular oxygen while such a competition cannot be achieved in the homogeneous solution even at high O₂ concentrations. Experimentally, this has been demonstrated, for example, by the fate of the *CHCl-CCl₃ radical generated upon oxidative C-H cleavage from 1,1,1,2-tetrachloroethane. Direct oxygen addition to this species yields the 'OOCHCI-CCI₃ peroxyl radical which eventually degrades into CCI₃COOH. After rearrangement (*CHCl-CCl₃ \rightarrow CHCl₂-CCl₂*) and subsequent peroxidation the then formed CHCl₂-CCl₂OO* peroxyl radical ends up in a completely different acid, namely, CHCl₂COOH. It could further be deduced that the 1,2-chlorine shift occurs via a bridged mechanism without transient liberation of the chlorine atom, thereby rendering an alternatively possible chlorine elimination/readdition mechanism an unlikely event. Finally, a marked pH dependence of the product distribution in both the γ -radiolytic and photocatalytic system is suggested to reflect acid/base catalyzed hydrolysis processes en route of the radical degradation to their final products.

Introduction

The redox-initiated degradation of halogenated organic compounds is known to generally proceed via free-radical mechanisms. This has been demonstrated, for example, for the biochemical process of metabolism¹ and many radiation chemical studies.²⁻¹⁴ The involvement of radicals has also been implied in a recent detailed study on the photocatalytic degradation of such substrates en route to mineralization.¹⁵ The fact that, for example, chlorinated organic compounds are ultimately degraded into CO₂ and HCl upon photocatalysis has already been shown in many earlier investigations.¹⁶⁻³³ This latter aspect is, of course, of particular interest in view of the environmental hazard most halogenated organic compounds represent. The underlying chemistry can be rationalized on the basis of the redox processes initiated upon illumination of semiconducting material.³⁴⁻⁵¹

The involvement of radicals appears to apply already for the early steps in a photocatalytic process. For the oxidation of substrates at TiO_2 surfaces, for example, the question had been raised whether this proceeds directly by valence band holes or goes through an intermediary formation of surface adsorbed hydroxyl radicals.³⁴⁻⁴⁸ In our recent study on the oxidative degradation

of chlorinated ethanes¹⁵ we could provide good supporting evidence that the initiating step was indeed the generation of adsorbed hydroxyl radicals

$$\equiv \text{Ti-OH}^- + h_{\text{VB}}^+ \rightarrow \equiv \text{Ti-OH} \quad [^{\bullet}\text{OH}_{\text{ads}}] \quad (1)$$

which preceded the actual oxidation of the substrate

>C(Cl)-C(H)< +
$$OH_{ads} \rightarrow$$
 >C(Cl)-C'< + H₂O (2)

Only when the organic compounds did not provide suitable C-H bonds for this hydrogen abstraction process could the oxidation occur through the, energetically apparently less favorable, direct valence band hole reaction.^{15,3}

Assignment of the underlying radical mechanism of the mineralization process became possible by comparison of the photocatalytic results with those from γ -radiolysis. The suitability of this complementary approach, in general, has been pointed out already in a number of cases.^{28,35,49-51} In our particular system the γ -radiolytic oxidation of the halogenated compounds occurs in analogy to reaction 2, although with freely diffusing hydroxyl radicals.^{10,15} Rationalization of the overall mechanism has in particular been based on the qualitative identity of the products generated by these two complementary methods: organic acids, aldehydes, fragmentation products, CO₂, and HCl. The formation of all these products can directly be related to and understood in terms of the well-known and documented chemistry of peroxyl radicals, in general.52,53

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Influence of TiO₂ Surface on 1,2-Chlorine Shift

Our recent comparative study¹⁵ has indicated, perhaps not surprisingly, that certain differences may exist between the heterogeneous photocatalytic and homogeneous γ -radiolytic systems with respect to relative reaction kinetics and, consequently, quantitative product distributions. A more detailed study is now presented in this paper in order to further evaluate on the influence of the TiO₂ surface on certain aspects in connection with the photocatalysis of chlorinated ethanes. As a "marker" a particular reaction has been chosen, namely, a rearrangement reaction occurring in β -chloroethyl radicals, a process which is qualitatively well-known from organic radical chemistry.^{15,54-71} Schematically this 1,2-chlorine shift is depicted in eq 3.

$$\begin{array}{cccccccccc} C & & C \\ I & & I \\ C_{\beta} - C_{\alpha} & \longrightarrow & C_{\beta} - C_{\alpha} & & C_{\beta} - C_{\alpha} \end{array}$$
(3)

Although there is no doubt that this reaction involves a radical, certain details of the actual rearrangement mechanism are still not fully understood. Thus only few and, furthermore, conflicting data are available on how fast this process occurs. Skell,^{66,67} for example, has estimated the rate constant k_r for the rearrangement CCl₃-C°ClH \rightarrow °CCl₂-CCl₂H from product yields to be >10⁸ s⁻¹ (even at <-140 °C)⁶⁴ which differs by orders of magnitude from the figure of 1.8×10^4 s⁻¹ evaluated by Gasanov⁶⁸ from spin-trap experiments. Our present study will provide some information on this question demonstrating at the same time the significant influence the TiO₂ surface may exert on the reaction kinetics.

Another problem our data allow us to address is concerned with the rearrangement mechanism as such. In some studies the 1,2-chlorine shift has been postulated to involve a bridged transition state^{57-60,65} (as shown in eq 3) while others rather consider an elimination/re-addition sequence^{61,62} as formulated in eq 4 for

$$\begin{array}{ccc} \text{Hal} & & \text{Hal} \\ \overset{1}{c}_{\beta} - C_{\alpha} \cdot & \longrightarrow & \left[-C_{\beta} = C_{\alpha} + \text{Hal} \cdot \right] & \longrightarrow & \cdot C_{\beta} - \overset{1}{C}_{\alpha} & (4) \end{array}$$

a general 1,2-halogen shift. The latter could clearly be envisaged for the migration of bromine atoms considering the fast dissociation of Br[•] from β -bromoethyl radicals^{9,11} and well-known (re-) addition of bromine to alkenes. Our results will show that this mechanism does, however, apparently not apply to the chlorine shift.

Our experimental methods of choice for these investigations have been again photocatalysis in heterogeneous TiO_2 suspensions and radiation chemistry of homogeneous solutions which have proven to be excellently complementary and thus most informative techniques.^{15,35,36}

Experimental Section

The experimental techniques used, the measurement of data, product analysis, and evaluation of the results have been described already in detail in a recent publication¹⁵ and some general methodological papers.^{10,72-75} Therefore, only some essential features will briefly be mentioned.

The titanium dioxide, used for the photocatalysis, was as a mixture of 80% anastase and 20% rutile obtained from Degussa (P25). Its average surface area amounted to 55 m²/g. 1,2-Dichloroethane (1,2-DCE), 1,1,1-trichloroethane (1,1,1-TriCE), 1,1,2-trichloroethane (1,1,2-TriCE), 1,1,2,2-tetrachloroethane (1,1,2,2-TetCE), and 1,1,1,2-tetrachloroethane (1,1,1,2-TetCE) were obtained from Aldrich. All organic compounds were of highest commercially available grade and were distilled once more prior to use. Their purity was controlled by gas chromatography.

The illumination apparatus for photo-catalysis was composed of a XBO Xe lamp (450 W, Müller, Electronic and Optic, FRG) equipped with a 15-cm water filter, to remove IR radiation to the utmost extent, and an illumination cell mounted with optically flat quartz entry and exit windows. During the illumination process the samples were stirred magnetically.

The UV light intensity was measured using Aberchrome 540 as chemical photodosimeter.⁷² The Aberchrome 540 (Aberchromics Ltd. USA) solution (>5 \times 10³ M) was irradiated with monochromatic light (Krator Polytec, GM 252); the respective

photoproducts at various time intervals were determined by their optical absorption at 494 nm (Varian Super Scan 3).

The γ -irradiations were carried out in the field of a ⁶⁰Co source of the Hahn-Meitner Institute Berlin. Dose rates were determined using Fricke dosimetry.⁷³

Identification and quantitative analysis of ionic products were performed by a high-performance ion chromatography unit (Dionex 2010i), which was equipped with a HPLC-AS4 anionexchange column, fiber suppressor, and conductivity detector.^{15,75} The eluent consisted of a mixture of NaHCO₃ and Na₂CO₃, 1.4 $\times 10^{-4}$ and 1.12 $\times 10^{-4}$ M, respectively. Analysis was generally based on comparison with authentic samples.

All experiments have been carried out at room temperature. Experimental error limits are $\pm 10\%$ (unless specifically stated).

Results and Discussion

1. Formation of Monochloroacetic Acid from 1,1,1-Trichloroethane. Oxidative degradation of 1,1,1-trichloroethane (1,1,1-TriCE) in an oxygen-containing environment leads to the formation of monochloroacetic acid (MCAA) as has been shown and discussed in detail in a previous study of ours.¹⁵ The underlying mechanism for the formation of this particular acid is summarized in eqs 5–10. As far as halogenated peroxyl radicals

$$CH_3CCl_3 + OH \rightarrow CH_2 - CCl_3 + H_2O$$
 (5)

$$\cdot CH_2 - CCl_3 \xrightarrow{\circ} CH_2Cl - CCl_2 \cdot (6)$$

$$CH_2Cl-CCl_2 + O_2 \rightarrow CH_2Cl-CCl_2OO$$
(7)

$$2CH_{2}Cl-CCl_{2}OO^{\bullet} \rightarrow 2CH_{2}Cl-CCl_{2}O^{\bullet} + O_{2}$$
(8)

$$CH_{2}CI - CCI_{2}O^{*} \rightarrow CH_{2}CI - CCIO + CI^{*}$$
(9)

$$CH_2CI-CCIO + H_2O \rightarrow CH_2CI-COOH + HCl$$
 (10)

are concerned, both their formation and subsequent fate are well documented^{1-14,76-78} and furthermore based on the known chemistry of peroxyl radicals in general.^{52,53} An essential aspect to explain the MCAA formation in our particular (and several corresponding) cases is that a radical rearrangement (eq 6) is required prior to the oxygen addition to the C-centered radical (eq 7). It may further be mentioned that in the presence of suitable H donors the oxyl radical CH₂Cl–CCl₂O[•] may be reduced in a competing process with reaction 9. The thus resulting CH₂Cl– CCl₂OH would, however, also end up as MCAA upon hydrolysis.

In photocatalysis, the initiating C-H bond cleavage is achieved by adsorbed hydroxyl radicals as formulated in reaction 2. Such reactions were performed by illumination of aqueous, pH 5-6, suspensions containing 3×10^{-3} M 1,1,1-TriCE, 1.25 g/L TiO₂ (P25), and various concentrations of oxygen. In air-saturated suspensions, illuminated for 3 min with polychromatic light (WG 295 filter), MCAA was formed with a yield of 32.5 μ M in agreement with our previous investigation.¹⁵

Initiation by freely diffusing hydroxyl radicals was achieved by radiolysis of aqueous solutions containing 3×10^{-3} M 1,1,1-TriCE and being saturated with N₂O/O₂ mixtures of varying ratio. Under this experimental condition about half of the 'OH are formed directly as result of the water irradiation

$$H_2O \xrightarrow{\gamma \text{-irradiation}} e_{aq}^- + {}^{\circ}OH + \dots \qquad (11)$$

while the other half results from subsequent chemical conversion of hydrated electrons through the reaction

$$e_{aq}^{-} + N_2 O + H_2 O \rightarrow OH + OH^{-} + N_2$$
 (12)

In the presence of high concentrations of N_2O , hydroxyl radicals are practically the only important radical species for primary reaction with added solutes.⁷⁴ (At lower N_2O/O_2 ratios direct scavenging of hydrated electrons by the oxygen has to be taken into account.)

The yield of monochloroacetic acid obtained from γ -irradiated N₂O/O₂ (4:1 v/v) solutions containing 3 × 10⁻³ M 1,1,1-TriCE amounted to 0.3 μ M per joule absorbed energy, or G(MCAA) = 2.9 ± 0.3.¹⁵ (The term G denotes the radiation chemical yield

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and represents the number of species/molecules generated/destroyed/converted per 100 eV of absorbed energy.) This corresponds to approximately half of the 'OH radicals available in such solutions (0.62 μ M J⁻¹, or G = 6) and indicates the occurrence of additional reaction pathways such as C-C breakage somewhere along the radical degradation route.^{10,15}

Another possibility to generate freely diffusing hydroxyl radicals is provided by photoinduced decomposition of H_2O_2 according to reaction 13. Hydrogen peroxide is known to be one of the major

$$H_2O_2 \xrightarrow{n\nu} 2^{\bullet}OH$$
 (13)

products generated upon illumination of aqueous TiO₂ suspensions^{32,36} and therefore, via eq 13, may contribute to the oxidative degradation of the halogenated compounds. In order to test this possibility, an aqueous solution of 3×10^{-3} M 1,1,1-TriCE and 10^{-3} M H₂O₂ was subjected to photolysis and MCAA was, indeed, identified as major product. (The investigation has been restricted, however, to a qualitative identification of the acid in this case.)

Corresponding reactions and considerations apply to the formation of organic acids from other chlorinated ethanes. In addition to the scheme given in reactions 5–10, it must only be noted that, whenever the peroxyl carbon carries at least one hydrogen atom, another bimolecular decay mode, namely the so-called Russell mechanism, 10,15,52,33 may operate and, in fact, even take over instead of reaction 8. This involves dimerization of two peroxyl radicals and hydrogen transfer in a cyclic tetroxide structure. The final products then constitute the formal result of a disproportionation reaction as formulated in eq 14. Hy-

$$2R-CHClOO^{\bullet} \rightarrow [tetroxide] \rightarrow R-CClO + R-CHClOH + O_2 (14)$$

drolysis of the chlorinated molecular products generated via this pathway would, of course, yield not only acid but also the corresponding aldehyde. It is important to recognize that the peroxyl carrying carbon atom must be substituted with at least one chlorine atom for any possible acid formation.^{10,15,76}

The necessary "blank" experiment, i.e., illumination of just an aqueous solution of 1,1,1-TriCE (or any other chlorinated ethane) in the absence of TiO₂ and/or H₂O₂ for up to half an hour, did not yield any MCAA (or corresponding product), indicating that direct photolysis of the chlorinated ethanes did not go into effect at the time scale of our present experiments.

2. Dependence on O_2 Concentration. Figure 1 presents the influence of the O_2 concentration on the yield of MCAA obtained from 1,1,1-TriCE for γ -radiolysis and photocatalysis. The data refer to solutions of 3×10^{-3} M 1,1,1-TriCE in water or TiO₂ suspensions saturated with N₂O/O₂ (Figure 1a) or N₂/O₂ mixtures of various molecular ratios (Figure 1b), respectively. (For the calculation of the actual oxygen concentration a linear relationship is assumed between the partial oxygen pressure and dissolved oxygen, i.e., 1.4×10^{-3} M in oxygen-saturated aqueous systems.)

Irrespective of the irradiation method, the MCAA yield first rises with oxygen concentration from zero to a maximum value proving unambiguously the involvement of oxygen in the formation mechanism of the acids. At higher oxygen concentrations then significant differences are noted between the two methods.

 γ -Radiolysis. For the γ -irradiated system the MCAA yields (Figure 1a) assume a practically constant level of G(MCAA) = 3.2 ± 0.2 already at low O₂ concentrations. Corrections for the O₂ + e_{aq}⁻ \rightarrow O₂⁻⁻ reaction, competing with N₂O + e_{aq}⁻ + H₂O \rightarrow 'OH + OH⁻ + N₂ (and being of significance, i.e., exceeding the experimental ±10% error limit, only at >0.6 mM, i.e., >50 vol % O₂), have been made on the basis of the documented rate constants for these two reactions.⁷⁷

Corresponding observations with respect to the oxygen concentration dependence of products have been made for the γ radiolysis of the tetrachlorinated ethane, 1,1,1,2-TetCE (N₂O/O₂ saturated soutions). In this case dichloroacetic acid (DCAA) is the only identifiable acid and was also found to be generated at constant yield within the higher ($\geq 0.2 \text{ mM}$, $\geq 15 \text{ vol }\%$) oxygen



Figure 1. Yields of monochloroacetic acid (MCAA) as a function of oxygen concentration from 1,1,1-trichloroethane (1,1,1-TriCE). (a) γ -Radiolysis of aqueous, pH 4, N₂O/O₂ (various vol % ratios) solutions of 3×10^{-3} M 1,1,1-TriCE. (b) Photocatalysis of aqueous, pH 5, suspensions of 1.25 g/L TiO₂ and 3×10^{-3} M 1,1,1-TriCE, saturated with N₂/O₂ mixtures (various vol % ratios); illuminated with polychromatic light for 3 min; WG 295 filter.

concentration region. The formation of DCAA is rationalized in terms of a rearrangement of the primary radical generated from $CH_2CI-CCI_3$ upon oxidative C-H cleavage

$$CHCl-CCl_3 \xrightarrow{\circ} CHCl_2 - CCl_2$$
(15)

followed by reaction of the rearranged radical with oxygen

$$CHCl_2 - CCl_2 + O_2 \rightarrow CHCl_2 - CCl_2OO^{\bullet}$$
(16)

and subsequent processes analogous to eqs 8-10 to yield the acid. The measured DCAA yield of 0.37 μ M J⁻¹ (or G = 3.6)¹⁵ is also lower than the yield of initiating 'OH radicals (0.62 μ M J⁻¹; G = 6). This has been explained by C-C cleavage of the oxyl radicals formed along the degradation route of the peroxyl radicals.¹⁵

It is specifically noted that upon γ -radiolysis of both 1,1,1-TriCE and 1,1,1,2-TetCE no C₂-products could be found which would originate from direct peroxidation of the unrearranged radicals, 'CH₂-CCl₃ and 'CHCl-CCl₃, respectively. (For possible products from the latter see below.)

These findings clearly demonstrate that under the condition of γ -radiolysis, i.e., in homogeneous solution, the rearrangement process (as formulated in eqs 6 and 15) must be fast compared with the oxygen uptake by the unrearranged radicals.

Photocatalysis. A noticeable difference compared with the radiolytic results shows up for the photocatalytic set of experiments (Figure 1b). Thus, an efficient formation of MCAA requires higher oxygen concentrations than in the homogeneous solution of the γ -radiolysis system (in fact, higher than air saturation) and, furthermore, the MCAA yield decreases markedly after reaching a pronounced maximum at ca. 0.4 mM (30 vol %) O₂.

For the initial part of the curve several reasons can be forwarded. Firstly, the kinetics of the acid formation may be slowed down due to an actually lower O_2 concentration at the TiO₂ surface than in the bulk of the solution, e.g., by blocking of adsorption sites by 1,1,1-TriCE. Secondly, scavenging of conduction band electrons (e_{CB}) may be insufficient at lower oxygen concentrations. This process is, however, a necessary prerequisite to ensure a long enough lifetime of the valence band holes (with respect to electron/hole recombination) for the initiation of the halocarbon



Figure 2. Yields of di- and trichloroacetic acid (DCAA and TriCAA, respectively) from photocatalysis of aqueous, pH 5, suspensions of 1.25 g/L TiO₂ and 3×10^{-3} M 1,1,1,2-tetrachloroethane (1,1,1,2-TetCE), saturated with N₂/O₂ mixtures (various vol % ratios); illuminated with polychromatic light for 5 min; WG 295 filter.

oxidation. Although our present results do not allow to distinguish between these (and/or possibly still other) reasons, they, nevertheless, suggest the importance of TiO_2 -specific parameters on the quantitative product yields.

In order to explain the decrease in MCAA yield observed at higher O₂ concentrations one might again, i.e., in view of the γ -radiolysis results discussed above, envisage an increased scavenging of electrons (here e_{CB}⁻) by oxygen. However, other than in the γ -irradiated solutions, the competing scavenger N₂O is not present in the TiO₂ system, and the only other substrate oxygen could compete with for e_{CB}⁻ is the chlorinated ethane itself. Reduction of the latter can, however, not be achieved by e_{CB}⁻ due to the too low redox potential of the conduction band electrons.¹⁵ Any scavenging of e_{CB}⁻ by oxygen would, therefore, not constitute a competition and consequently not serve as a cause for the observed decrease in MCAA yield. As stated above, the removal of e_{CB}⁻ by O₂ rather exerts a promotional effect on the yield of oxidation products.

Another, perhaps more plausible explanation for the decrease in MCAA yield could be an increased blocking of surface sites by oxygen at the expense of 1,1,1-TriCE, an argument discussed already in connection with the photocatalytic MCAA formation from 1,1,2-TriCE.¹⁵ The observed decrease in MCAA yield in the latter system was, however, considerably smaller ($\leq 15\%$ between 20 and 100% oxygen). The difference between 1,1,1-TriCE and 1,1,2-TriCE could then be explained if the former was more tightly bound to the TiO₂ surface and less easily replaceable by oxygen. This may not be an unrealistic assumption because in 1,1,2-TriCE polarizable C-Cl bonds are present at both carbon atoms while in 1,1,1-TriCE they are concentrated on one carbon. The pronounced oxygen dependence for the acid formation from 1,1,2-TetCE cannot, however, be rationalized anymore on this consideration.

A much more satisfactory explanation is, in fact, based on the findings obtained with the tetrachlorinated ethane 1,1,1,2-TetCE. Upon photocatalysis of this substrate in the heterogeneous TiO_2 system two acids are formed as products, namely, dichloroacetic acid (DCAA) and trichloroacetic acid (TriCAA). TriCAA arises from degradation of 'OOCHCl-CCl₃, i.e., requires oxygen uptake by the original primary, i.e., unrearranged radical.

$$\cdot CHCl - CCl_3 + O_2 \rightarrow \cdot OOCHCl - CCl_3$$
(17)

As shown in Figure 2, the respective DCAA and TriCAA yields are complementary to each other: the higher the oxygen concentration, the higher the TriCAA yields, and the lower the DCAA yields. This suggests a competitive scheme with respect to the oxygen addition between the rearranged radical (eq 16) and the original radical (eq 17).

By the same token, the results obtained upon photocatalysis of 1,1,1-TriCE would find their explanation by a competition



Figure 3. Kinetic analysis of DCAA formation from photocatalysis of 1,1,1,2-TetCE as function of oxygen concentration according to eq II.

between rearrangement of the original $^{\circ}CH_2$ -CCl₃ radical (eq 6) and direct oxygen uptake by this primary species (eq 18). Further

$$CH_2 - CCl_3 + O_2 \rightarrow OOCH_2 - CCl_3$$
 (18)

degradation of the peroxyl radical formed in this latter reaction would not yield any acid but only lower oxidation state compounds, namely, alcohol (CCl₃CH₂OH) and aldehyde (CCl₃CHO-H₂O). Both could qualitatively be identified at higher oxygen concentrations; satisfactory quantitative measurements were, however, hampered by too low yields.

3. Rate Constant for Rearrangement. Kinetic Analysis. Analysis of the competitive scheme on the basis of the oxygen dependences displayed in Figures 1 and 2 (at higher O_2 concentrations, i.e., >0.4 mM, >30 vol %) allows to estimate the rate constant of rearrangement in the heterogeneous TiO₂ system. Applying simple competition kinetics, the actual yield of the acid resulting from rearrangement, A_r , amounts to

$$[A_{r}] = [A]_{0} \times \frac{k_{r}}{k_{r} + k_{p}[O_{2}]}$$
(I)

 $[A]_0$ represents the total yield of acids formed, i.e., from both the rearranged and unrearranged radical. The rate constants k_r and k_p refer to the rearrangement reaction and the oxygen uptake by the primary, i.e., unrearranged radical, respectively. This equation converts into

$$\frac{1}{[A_r]} = \frac{1}{[A]_0} \left(1 + \frac{k_p}{k_r} [O_2] \right)$$
(II)

The results obtained for the DCAA formation from 1,1,1,2-TetCE, for example, and analyzed according to eq II are shown in Figure 3. A reasonably good straight line is obtained for the $1/[A_r]$ vs $[O_2]$ relationship. Taking $[A]_0 = 70 \ \mu$ M (see Figure 2), a value of $k_p/k_r = 800 \ (\pm 100)$ is derived from the slope. The rate constant for the addition of oxygen to the °CHCl-CCl₃ radical ($k_p = k_{17}$) could not be determined in the heterogeneous system (due to interference of fast rearrangement). It may, however, be taken as $10^9 \ M^{-1} \ s^{-1}$ in analogy to measured values for this kind of reaction of many similar chlorinated ethyl radicals in homogeneous aqueous solution.⁷⁸ On this basis the rate constant for the rearrangement of °CHCl-CCl₃ to CHCl₂-CCl₂ in the heterogeneous TiO₂ system would be derived at $k_1 = k_{15} = 1.25 \times 10^6 \ s^{-1}$.

A corresponding analysis for the TriCAA formation gave less satisfactory results. Particularly for the lower oxygen concentration range with low TriCAA yields the, in this case, requested linear relationship between 1/[TriCAA] and $1/[O_2]$ shows considerable curvature. Estimates derived from the high oxygen concentration points, i.e., those providing the highest TriCAA yields and highest analytical accuracy, give k_r values in the range of $(1.0-2.5) \times 10^6 \text{ s}^{-1}$ in good agreement with the above number.

Analysis of the decrease in MCAA yield from 1,1,1-TriCE (Figure 1) according to eq II, and taking again $k_p = 10^9 \text{ M}^{-1} \text{ s}^{-1}$,

gives $k_r = k_9 = 4.3 \times 10^5 \text{ s}^{-1}$ for the rearrangement of $^{\circ}\text{CH}_2\text{-CCl}_3$ to CH₂Cl-CCl₂[•].

These rate constants for the rearrangement reactions in the photocatalytic system differ significantly from those apparently applicable in homogeneous solution. In the latter system our γ -radiolysis data show clearly that oxygen addition to °CHCl-CCl₃ and °CH₂-CCl₃ cannot compete with rearrangement of these radicals, i.e., $k_r \gg k_p[O_2]$ even at the highest oxygen concentrations. This means that, under homogeneous conditions, k_r should be at least of the order of 10^8 s^{-1} or higher, in agreement with the published estimate by Skell.^{66,67} On the other hand, our results would not support the very low values evaluated from the spin-trapping experiments.⁶⁸

Rationalization of the Rate Constants. Which arguments can be forwarded to explain the apparently much lower rate constant for rearrangement in the heterogeneous system? Clearly, it must be remembered that our experiments did not yield k_r directly but only the ratio between rearrangement and primary oxygen addition, i.e., $k_r/(k_p[O_2])$. The low value for k_r may therefore not only reflect a kinetically hampered rearrangement reaction but equally an enhanced oxygen reaction. One trivial reason in favor of the latter would be a higher oxygen concentration at the TiO_2 surface as compared with the bulk of the solution. However, the surface concentration of oxygen would have to be higher by practically 2 orders of magnitude to account for the observed data, which is hard to believe and lacks any evidence in the scientific literature. In fact, there are reports that oxygen is not strongly adsorbed at all at semiconductor surfaces in contact with aqueous electrolytes.⁷⁹ Another possibility to explain a low value of k_r would be an enhanced rate constant k_p in the heterogeneous system. Since activation energies do not seem to play any significant role in the oxygen addition^{15,78} this would then only be understandable in terms of a significantly enhanced diffusion of the oxygen and/or primary radical to and at the TiO_2 surface. This, however, seems unrealistic considering that the diffusion would have to be faster by several others of magnitude than under homogeneous bulk conditions.

A much more reasonable explanation for the low k_r value would indeed be a relative slowdown of the rearrangement process at the TiO₂ surface. It can be envisaged that translocation of the chlorine atom over the C–C bridge in order to be kinetically favorable demands a certain steric configuration. Because of the interaction between radical and surface, this may, however, not be achievable in the adsorbed and therefore sterically presumably hindered state. Additional energies required for the change in hybridization of both the chlorine-donating and -accepting carbon atom (sp² to sp³, and vice versa) in the adsorbed state as compared to the free radical, and/or spin delocalization into the surface may also contribute. It seems that the mechanistically delicate process of 1,2-chlorine shift with its specific steric demands is indeed very sensitive to surface-specific parameters.

An additional complicating factor in the kinetic analysis and for an unambiguous assignment of rate constants solely on the basis of product yields could be surface specific changes in the kinetics of any other reaction involved as well (see e.g., 1,1,2-TriCE example below). Last, but not least, a possible reversibility of the rearrangement reaction may be taken into consideration, but our results do not provide any conclusive evidence for it.

Any discussion of absolute numbers for the rate constants needs, of course, to be done in view of the practically two-dimensional reaction area for those processes occurring at the TiO_2 surface. A quantitative interpretation of the derived rate constants for the rearrangement reaction may therefore still be open for adjustments. Fact is, however, an indisputable difference between the homogeneous and heterogeneous systems and it seems that, in our case, this is primarily associated with the 1,2-chlorine rearrangement reaction.

4. Acid Formation from 1,1,2,2-TetCE. Photocatalytic oxidative degradation of 1,1,2,2-TetCE in air-saturated TiO₂ suspensions yields only one type of organic acid, namely, dichloroacetic acid (DCAA).¹⁵ This earlier finding has now been substantiated with corresponding γ -radiolysis experiments. For both, the γ -radiolytic

and photocatalytic system no significant changes in DCAA yields were observed with varying oxygen concentration.

The formation of DCAA is initiated by the reaction of 1,1,2,2-TetCE with hydroxyl radicals which exclusively leads to $^{\circ}CCl_2$ -CHCl₂ radicals in the first step. Oxygen addition to these primary C-centered radicals and subsequent degradation of the thus formed $^{\circ}OOCCl_2$ -CHCl₂ peroxyl radical constitute the further steps en route to CHCl₂-COOH. Although the primary radical contains two chlorine atoms at the β -carbon (relative to the radical carbon), a possible 1,2-chlorine shift

$$CCl_2 - CHCl_2 \not \rightarrow CCl_3 - CHCl^{\bullet}$$
 (19)

does not seem to take place since oxygen addition to CCl_3 -CHCl[•] and subsequent degradation of the CCl_3 -CHClOO[•] peroxyl radical would lead to trichloroacetic acid, CCl_3 -COOH. Such a product was, however, not at all observed.

This cannot simply be rationalized in terms of a lower number of chlorine atoms at the nonradical carbon in CCl_2-CHCl_2 compared with CH_2-CCl_3 or CHCl--CCl_3. The CH_2-CHCl_2 radical, for example, contains two β -chlorine atoms like CCl_2 -CHCl_2 but, other than the latter, readily rearranges (to CH_2Cl-CHCl' which eventually degrades to monochloroacetic acid). The important parameter rather seems to be the relative degree of chlorination at both carbon atoms. Chlorine atom migration occurs only if the accepting radical carbon is less chlorinated than the donating carbon. Since chlorine atoms are strong electrophiles, they are expected to prefer that site which is comparatively less crowded with the electron-withdrawing chlorine substituents. In addition, resonance stabilization of the various radicals, operating in favor or disfavor of the rearrangement, may also contribute to the product distribution.

It can easily be envisaged that equal chlorine substitution, as in the ${}^{\circ}CCl_2-CHCl_2$ radical derived from 1,1,2,2-TetCE, would render the driving force for a chlorine shift practically zero. Furthermore, the resulting radical CCl_3-CHCl° would be the subject of easy back-rearrangement to yield again the original radical (eq 15). Reaction 19 would, therefore, constitute an uphill process from the energetic point of view. The fact that no rearrangement product could be detected even at low oxygen concentrations shows that such an uphill rearrangement has, indeed, no chance to compete with the oxygen addition to the primary radical.

It is interesting to note though that a $CCl_2-C(OH)Cl_2$ radical generated, e.g., by OH addition to tetrachloroethene and which contains a hydroxyl group rather than an H atom in addition to the chlorine substituents seems to undergo rearrangement to $CCl_3-C(OH)Cl^*$. The peroxyl radical $CCl_3-C(OH)(Cl)OO^*$ derived therefrom would be a direct precursor of the observed acid CCl_3-COOH .^{80,81} This indicates that the overall energetics of the chlorine shift are not only controlled by the relative chlorine population but also to a significant extent by the nature of the other substituents.

5. Acid Formation from 1,1,2-TriCE. Oxidative C-H cleavage from 1,1,2-TriCE may occur at both carbon atoms yielding two different radicals.

$$CHCl_2-CH_2Cl + OH \rightarrow H_2O + CHCl_2-CHCl$$
(20a)

$$\rightarrow H_2O + {}^{\bullet}CCl_2 - CH_2Cl \qquad (20b)$$

In light of the above considerations, rearrangement may only be expected for the $CHCl_2$ - $CHCl^*$ radical with a 2:1 chlorine substitution at the two carbons. Rearrangement would, however, yield an identical species and would therefore escape detection.

The other primary radical formed from 1,1,2-TriCE, $^{\circ}CCl_2$ -CH₂Cl, is not expected to rearrange as its transformation into CCl₃-CH₂[•] would energetically again be an uphill process. In agreement with this, no chloral (an expected product from CCl₃-CH₂[•] after oxygen uptake and hydrolysis) was detectable. This explains why there is no significant oxygen dependence on the MCAA yield from 1,1,2-TriCE (reported in our earlier publication)¹⁵ as compared with the 1,1,1-TriCE and 1,1,1,2-TetCE examples. (A comparatively small decrease of MCAA from 1,1,2-TriCE at high oxygen concentrations has been suggested to reflect increased blocking of surface sites and possible interferences of $O_2^{\bullet-}/H_2O_2$.)¹⁵

Since the radicals CHCl₂-CHCl^{*} and ^{*}CCl₂-CH₂Cl exclusively yield acids of different kind (DCAA and MCAA, respectively) it is possible to distinguish between reactions 20a and 20b. The formations of DCAA and MCAA are thus representative for the abstraction of a secondary and tertiary hydrogen atom, respectively. Energetically the latter should be favored, and for γ -radiolysis the measured yields, $G(DCAA) = 1.0 (0.11 \,\mu\text{M J}^{-1})$ and $G(MCAA) = 2.5 (0.26 \,\mu\text{M J}^{-1})$,¹⁵ are in good accord with this expectation. For any quantitative assessment of the initial abstraction ratio it must be noted though that the acid yields account only for ca. 60% of the initiating hydroxyl radicals. From the remainder, the C₁ products from C-C cleavage, for example, cannot unambiguously be associated with a particular primary radical.

Most interestingly, the DCAA/MCAA ratio of ca. $4:3^{15}$ measured in photocatalysis is very different, indicating either a relatively too high DCAA yield or, correspondingly, a relatively too low MCAA yield as compared with the γ -radiolysis system. Our present data provide no further clues on this question but it seems more realistic to assume the latter, caused, for example, by surface specific side reactions of MCAA or its precursors. This comparison between γ -radiolysis and photocatalysis is quite informative in the sense that it clearly shows the value of such complementary studies and by demonstrating also the limits of extrapolation from the homogeneous to the heterogeneous system.

6. Rearrangement or Elimination/Readdition? How does the 1,2-chlorine shift occur? Is it a true rearrangement with a bridged transition state, 57-60,65 or an elimination-addition mechanism including the generation of free chlorine atoms (Cl[•])?^{61,62} In order to elucidate this question experiments were performed for the 1,1,1-TriCE system, for example, in which the presence or absence of free chlorine atoms was tested by scavenging reactions.

The actual experiments were performed with air-saturated solutions of 3×10^{-3} M 1,1,1-TriCE and 1×10^{-4} M 1,2-dichloroethene (CHCl=CHCl), pH ~ 5, illuminated with polychromatic light. The choice of a 1,2-chlorine substitution at the olefin was again made to ensure that scavenging of any free chlorine atom, possibly liberated in the rearrangement reaction (eq 6), would clearly be distinguishable from the products generated from either 1,1,1-TriCE or 1,2-dichloroethene alone.

In the case of an elimination/readdition mechanism, chlorine atoms would result by β -cleavage from the primary CH_2-CCl_3 radical formed upon oxidation of 1,1,1-TriCE (eq 21). Readdition

$$^{\bullet}CH_2 - CCl_3 \rightarrow CH_2 = CCl_2 + Cl^{\bullet}$$
(21)

of the chlorine to the thereby generated 1,1-dichloroethene (because of the directing forces exerted by the two chlorine atoms in the latter; eq 22) would yield the same radical as in the true

$$Cl^{\bullet} + CH_2 \Longrightarrow CCl_2 \rightarrow CClH_2 - CCl_2^{\bullet}$$
(22)

rearrangement process (eq 6). A free chlorine atom could, however, also add to the 1,2-dichloroethene (in this case with no preference for one particular carbon)

$$Cl' + CHCl = CHCl \rightarrow CHCl_2 - CHCl'$$
(23)

This reaction would, in fact, occur with even higher probability than reaction 22 because the 1,2-dichloroethene concentration (10^{-4} M) is much higher than that of photogenerated 1,1-dichloroethene.

Further degradation of the CHCl₂-CHCl[•] radical in the oxygen-containing aqueous environment would eventually yield dichloroacetic acid.

$$CHCl_2-CHCl^* + O_2 \rightarrow CHCl_2-CHClOO^* \rightarrow \rightarrow \rightarrow DCAA$$
(24)

Since DCAA is formed neither from 1,1,1-TriCE alone¹⁵ nor from 1,2-dichloroethene alone,⁸⁰ this acid would unambiguously be indicative for free chlorine atoms. The experimental result shows, however, no formation of DCAA at all which would discard this mechanistic possibility. The only organic acid observable is



Figure 4. (a) pH dependence of the formation of monochloroacetic acid (MCAA) upon photocatalysis of aqueous, air-saturated suspensions of 1.25 g/L TiO₂ and 3×10^{-3} M 1,1,1-TriCE; illuminated with polychromatic light for 3 min; WG 295 filter (pH's refer to preirradiation conditions). (b) pH dependence of the formation of monochloroacetic acid (MCAA) (\bullet) and CO₂ (O) upon γ -radiolysis of aqueous, N₂O/O₂ (4:1 v/v) saturated solutions of 3×10^{-3} M 1,1,1-TriCE.

monochloroacetic acid (MCAA), i.e., the product compatible with an intramolecular rearrangement and a presumably bridged intermediate. (An uncertainty would remain though if potentially free chlorine atoms were quantitatively scavenged by the TiO_2 surface.) For comparison, it is noted that a control experiment with free bromine atoms proved positive.⁸⁰ Br[•] atoms, known to be liberated from $CH_2Br-CH_2^{•,9}$ could be scavenged by $CH_2=$ CCl_2 to yield $CH_2Br-CCl_2^{•}$ which eventually ended up as $CH_2Br-COOH$.

7. **pH Dependence.** The pH dependence of rearrangement products has been studied in some detail for the MCAA formation from 1,1,1-TriCE. The results are displayed in Figure 4, a and b, for the photocatalytic and γ -radiolytic systems, respectively. In both cases the curves show minima at or near neutral pH (pH 7 and 6, respectively).

Higher yields in acid solutions could, in principle, be explained by the theoretically in fact predicted,^{70,71} possibility to establish a transition structure in which the transferred chlorine is protonated.



In consequence, the latter would become even more electrophilic than in the neutral bridge and this, in turn, would result in a higher rate constant for the rearrangement reaction (eq 6). The increased MCAA yields at low pH would thus go at the expense of the competing oxygen addition to the original radical (eq 18) (not leading to MCAA).

This model would, however, not explain the increase in MCAA yield observed on the basic side. The almost complementary formation of CO₂ as measured in the γ -radiolytic system with a maximum at pH 5–6, and included in Figure 4b, probably provides a more general clue. This C₁ product is a fragmentation product from the already oxygenated radicals (most likely oxyl radicals from the bimolecular peroxyl radical decay).^{10,15,76} The pH dependence can then be rationalized in terms of two competing decay routes of the peroxidized rearranged radical(s), one leading to the acid (here MCAA) and the other to the fragmentation

products (here CO_2). Both pathways include hydrolysis steps, and it is well-known that hydrolysis is generally accelerated by both acid and base. We conclude therefore, that those steps leading to the acids benefit in particular from hydrolysis, i.e., elimination of the chlorine substituents at an early stage of the reaction sequence. Hydrolysis occurring already within the rearranged peroxyl radical CH2Cl-CCl2OO* (favored by the electronegative peroxyl substituent)82 would thus yield hydroxyperoxyl radicals, CH₂Cl-CCl(OH)OO[•] or CH₂Cl-C(OH)₂OO[•], both of which are prone to HO₂[•] elimination.⁵³ The latter would directly lead to the acid

while HO₂[•] elimination from the former would yield the corresponding acetyl chloride, CH₂Cl-CClO, as additional intermediate. Slower hydrolysis, as it applies for the neutral pH range, would, on the other hand, provide the chance for the $CH_2Cl-CCl_2OO^4$ peroxyl radical to degrade into the corresponding oxyl radical. The latter, in its chlorinated form, CH₂Cl-CCl₂O[•], as well as in its hydrolyzed forms, CH₂Cl-CCl(OH)O[•] and CH₂Cl-C(OH)₂O[•] $[CH_2Cl-C(=0)O' + H_2O]$, would readily suffer β -cleavage. C-Cl bond breakage (in the not yet fully hydrolyzed species) would again directly yield MCAA while each fragment of the alternative C-C cleavage would result in CO₂.

The above considerations are based on the assumption that competitive decay modes of the rearranged radical are in operation for the formation of the acid of concern and of CO₂, respectively. In order to be conclusive we should therefore also consider the possible fate of the oxidized radicals derived from the primary, i.e., unrearranged CCl₃-CH₂ radical. To begin with, the corresponding peroxyl radical CCl₃-CH₂OO[•] would not give any acid.^{10,15,76} Furthermore, the oxyl radical CCl₃-CH₂O[•] (other than CCl₃-CCl₂O[•], CH₂Cl-C(OH)₂O[•], or CH₂Cl-COO[•]) is not particularly prone for a β -cleavage which happens practically only with tertiary oxyl radicals. $(CCl_3-CH_2O^{\bullet} may rather suffer a fast 1,2-hydrogen shift to yield CCl_3-C^{\bullet}H-OH.)^{83}$ Our study with 1,1,1-TriCE is therefore indeed conclusive in this respect.

C-C cleavage and CO₂ formation does not only occur in the γ -radiolytic system but also upon photocatalysis.^{15,76} A corresponding pH dependence is, however, associated with many uncertainties with respect to the interpretation of quantitative data because of onsetting mineralization of all products originally present or formed during the oxidative degradation at the TiO_2 .

The pH dependence shown in Figure 4a is reminiscent of the amphoteric character of the TiO₂ surface, and the minimum in MCAA yield production could accordingly be associated with the "zero point of charge" at around pH 6-7 of this material. In the light of our findings that, in the case of photocatalysis, the reactions of interest (rearrangement, oxygen uptake, and hydrolysis) occur at the surface it is, indeed, most reasonable to consider the acid-base properties of the TiO₂ surface for any quantitative evaluation of the product yields.

Conclusion

The investigation of an original problem in physical and theoretical organic chemistry, namely a 1,2-chlorine shift in radicals, by means of photocatalysis at TiO₂ and by γ -radiolysis has revealed a significant influence of the semiconductor surface on the reaction kinetics and the quantity of products. In particular, it provided some new and interesting insight into the mechanism of this rearrangement process. It was found, for example, that, in homogeneous solution, the 1,2-shift occurs much faster than the reaction of the unrearranged radical with oxygen substantiating those earlier reports which assign a rate constant of $>10^8$ s⁻¹ to this rearrangement reaction. In contrast, a much lower rate constant in the range of 10⁶ s⁻¹ has been derived for the heterogeneous system which could be associated with a hindrance of the rearrangement process at the TiO₂ surface. The results furthermore suggest that the 1,2 chlorine shift is indeed an intramolecular atom transfer proceeding most likely via a bridged

intermediate and does not operate via a chlorine elimination/ readdition mechanism. Finally, the study has demonstrated once more the complementary character of radiation chemical and photocatalytic methods for the investigation of radical related chemistry in general and for the environmentally interesting mineralization process of halogenated organic substrates, in particular.

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Carbon-Halogen Bond Dissociation on Copper Surfaces: Effect of Alkyl Chain Length

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Carbon-halogen bond dissociation in a series of straight-chain alkyl halides adsorbed on single crystal copper surfaces has been studied by high-resolution electron energy loss spectroscopy, temperature-programmed desorption, and work-function measurements. For two or more carbons in the alkyl chain, the rate of carbon-halogen (C-X) bond dissociation is independent of chain length, despite the fact that the heat of molecular adsorption (assuming a first-order preexponential factor of 10^{13} s^{-1} for desorption) increases at the rate of 1.3 ± 0.2 (kcal/mol)/CH₂ group. The combination of these two effects produces a sharp transition in the branching between desorption and decomposition as a function of alkyl chain length. For alkyl chlorides the surface reaction path switches from desorption to decomposition between C6 and C7; for the alkyl bromides the transition is between C_2 and C_3 . All of the alkyl iodides decompose. The C-X bond dissociation rates decrease in the order C-I > C-Br > C-Cl, and the activation energies for C-X bond scission are approximately 15% of the gas-phase bond energies in each case. The chain length dependence for the heat of adsorption suggests that the molecularly adsorbed alkyl halides bind with their carbon chains approximately parallel to the surface plane, while surface vibrational spectra indicate that the alkyl groups formed by carbon-halogen bond scission reorient to stand upright on the surface. The independence of the C-X bond dissociation rate on alkyl chain length suggests that reorientation of the carbon chain occurs after the transition state for C-X bond scission. The results are rationalized by using a modified Lennard-Jones picture of dissociative adsorption.

1. Introduction

Carbon-halogen bond dissociation on metal surfaces is a key step in synthetic processes such as the Grignard reaction¹ and the Rochow process,² yet surprisingly little is known about the details of this elementary surface reaction. In general, the reactivity of alkyl halides with metals decreases in the order iodides > bromides > chlorides, as might be expected from the gas-phase carbonhalogen bond energies: C-I \simeq 55 kcal/mol; C-Br \simeq 70 kcal/mol; C-Cl \simeq 85 kcal/mol. On the other hand, this qualitative reactivity trend reflects a competition between the rate of carbon-halogen bond dissociation and the rate of alkyl halide desorption from the metal surface. Bromomethane may be less reactive than iodomethane because it has a faster rate of desorption (lower heat of adsorption) as opposed to a slower rate of carbon-halogen bond dissociation. Based on the results to date, this is an open issue. For example, bromo- and chloromethane desorb molecularly intact from Pt(111) below 200 K, the temperature where the carboniodine bond in iodomethane dissociates.³⁻⁵ Perhaps the rates of C-Br and C-Cl dissociation are close to that for C-I dissociation and yet dissociation may not be observed because desorption predominates.

Alkyl chain length also has an effect on carbon-halogen bond dissociation on metal surfaces. For two or more carbons, lengthening the alkyl chain does not change the gas-phase carbon-halogen (C-X) bond energy,⁶ but it could affect the rate constant for dissociating the adsorbed C-X bond (for example, by constraining the C-X bond to a particular orientation with respect to the metal surface), and it certainly decreases the rate

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