

Simulation of Atmospheric Photochemistry in the Presence of Solid Airborne Aerosols

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Summary

A smog chamber for the simulation of tropospheric chemistry in the presence of aerosols was installed. Thermostating of lid and bottom of the cylindrical, vertically arranged vessel of 2.4 m^3 volume facilitates aerosol residence times of 1 day in the presence of simulated sunlight, and of 2 days in the dark. At initial mass concentrations up to 3 mg m^{-3} , the aerosols SiO_2 , TiO_2 , Fe_2O_3 , coal fly ash and NaCl are investigated in a photo-smog of NO_x and hydrocarbons. SiO_2 and fly ash show inert behaviour. The rate constants of OH, observed in the presence of these aerosols, agree well with literature values. In the smog chamber (and in a further 0.5 m^3 chamber) rate constants for further compounds are determined for the first time, among them the n-alkanes up to n-hexadecane. In the presence of TiO_2 , at 2 mg m^{-3} , concentrations of OH enhanced by one order of magnitude are observed, reaching levels of 10^8 cm^{-3} . In addition, a heterogeneous photodegradation occurs with an intensity inversely proportional to the vapour pressure of the hydrocarbons; for compounds, less volatile than n-hexane, the heterogeneous photodegradation surpasses the reaction with OH in the gas phase. A similar, possibly vapour pressure-dependent photodegradation is detected with low volatile aromatics in the presence of Fe_2O_3 . In the presence of NaCl aerosol, Cl atoms are formed, competing and surpassing the contribution of OH to the consumption of alkanes after a few hours. The contribution of these processes observed in a laboratory simulation experiment to tropospheric chemistry is discussed.

Zusammenfassung

Eine Smogkammer für die Simulation der troposphärischen Chemie in Gegenwart von Aerosolen wurde aufgebaut. Thermostatierung von Deckel und Boden der zylindrischen, senkrecht aufgestellten Kammer von $2,4 \text{ m}^3$ Volumen ermöglicht mittlere Aufenthaltsdauern des Aerosols im Schwebezustand von 1 Tag in Gegenwart von simuliertem Sonnenlicht und von 2 Tagen bei Dunkelheit. Bei Anfangsmassenkonzentrationen bis 3 mg m^{-3} werden die Aerosole SiO_2 , TiO_2 , Fe_2O_3 , Flugasche eines Kohlekraftwerkes und NaCl in Gegenwart eines Photosmogs aus NO_x und Kohlenwasserstoffen untersucht. SiO_2 und Flugasche weisen weitgehend inertes Verhalten auf. Die in Gegenwart dieser Aerosole gemessenen Geschwindigkeitskonstanten des OH-Radikals mit Kohlenwasserstoffen stehen im Einklang mit der Literatur. In der vorgestellten (und einer weiteren Smogkammer von $0,5 \text{ m}^3$ Volumen) werden die Reaktivitäten weiterer Stoffe, darunter der n-Alkane bis n-Hexadecan, erstmals bestimmt. In Gegenwart von TiO_2 bei 2 mg m^{-3} werden um eine Größenordnung, auf 10^8 cm^{-3} , erhöhte OH-Konzentrationen beobachtet, darüber hinaus ein heterogener Photoabbau, dessen Intensität umgekehrt proportional mit dem Dampfdruck der Kohlenwasserstoffe zunimmt. Bereits bei Stoffen mit geringerem Dampfdruck als Hexan überwiegt der heterogene Photoabbau gegenüber der Reaktion mit OH in der Gasphase. Ein ähnlicher, möglicherweise vom Dampfdruck abhängiger Photoabbau wird an Fe_2O_3 -Aerosol, jedoch nur für relativ schwerflüchtige Aromaten beobachtet. In Gegenwart von NaCl-Aerosol wird eine Bildung von Cl-Atomen beobachtet, die nach wenigen Stunden die OH-Radikale beim Abbau der Alkane übertreffen. Die Beiträge dieser im Labor beobachteten Phänomene zur Chemie der Troposphäre werden diskutiert.

Résumé

Afin de simuler la chimie de la troposphère en présence d'aérosols, une chambre a été construite. La température est maintenue constante à la base et au sommet d'un cylindre de $2,4 \text{ m}^3$ en position verticale, afin de garder l'aérosol en suspension pendant une journée en moyenne en présence d'une lumière solaire simulée, et pendant deux jours dans l'obscurité. Pour des concentrations initiales allant

jusqu'à 3 mg m^{-3} , on a étudié l'influence des aerosols SiO_2 , TiO_2 , Fe_2O_3 , des cendres volantes d'une centrale électrique à charbon, et du NaCl, en présence d'un photo-smog de NO_x et d'hydrocarbures. Le SiO_2 et les cendres volantes restent à peu près inactives. Les vitesses de réaction du radical OH avec les hydrocarbures, en présence de ces aerosols correspondent aux valeurs de la littérature. Les vitesses de réaction d'autres substances chimiques, y compris celles de n-alcane jusqu'au n-hexadecane sont déterminées pour la première fois dans la chambre de simulation présentée ci-dessus, ainsi que dans une autre chambre de $0,5 \text{ m}^3$. En présence de TiO_2 à 2 mg m^{-3} , des concentrations de OH dix fois plus élevées atteignant 10^8 cm^{-3} , sont observées. De plus une photodégradation hétérogène, dont l'intensité est inversement proportionnelle à la pression à vapeur de l'hydrocarbure a été observée. La photolyse hétérogène dépasse déjà la réaction avec OH dans la phase gazeuse pour des composés moins volatils que le n-hexane. Une photodégradation semblable, dépendant probablement de la volatilité, a été trouvée pour les aromatiques peu volatils, en présence de l'aérosol Fe_2O_3 . En présence de l'aérosol NaCl, des atomes de chlore se forment, et leur concentration dépasse en quelques heures celle des radicaux OH. La contribution de ces observations expérimentales à l'étude de la chimie de la troposphère est discutée.

1 Introduction

Atmospheric chemistry in the homogeneous gas phase appears to be reasonably well understood. Depending on the structure of the compounds, the photochemical conversion is mostly started by attack of OH and O_3 . To a minor extent NO_3 , HO_2 , O, and also Cl may contribute to these processes (1), although their portion may depend on light intensity, humidity and air pollution. For organic air pollutants, attack by O_3 is a major degradation path only with unsaturated organic compounds, containing activated olefinic double bonds (2); attack by OH is the major path with most other organics, containing either multiple C-C-bonds or abstractable H-atoms from C-H-

the peripheral equipment.

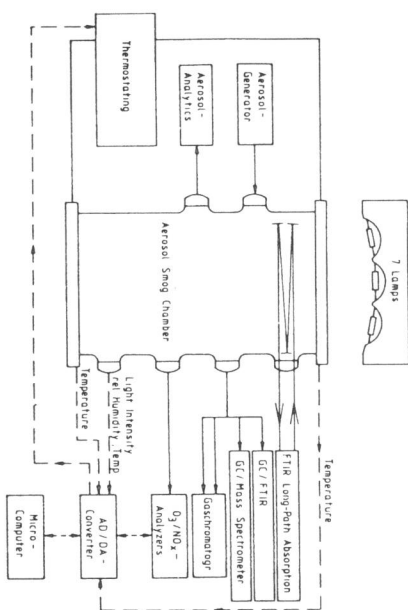


Fig. 2: Schematic diagram of the aerosol smog chamber with the solar simulator (top) and the peripherals.

The solar simulator consists of 7 medium pressure metal vapour lamps (HMI, 1200, Osram). It attains an intensity of three times that of the sun in Central Europe on a clear summer day at noon, with correspondingly adjusted spectral distribution /15/ by using a 2 mm glass sheet (Duran, Schott) as a cut-off filter. The infrared portion of the radiation from the 8 kW simulator is absorbed by a 3-cm water layer on the lid of the smog chamber and by a water-cooled black anodized aluminium bottom plate. For some (homogeneous gas phase) experiments a second, all-glass smog chamber (500 l volume) with similar properties is used. A microcomputer (9826, Hewlett Packard) controls the temperature gradient across the chamber by means of a cooling engine. A photosmog is generated in the chamber in the absence and presence of aerosols, by irradiating mixtures of NO_x (100 ppb $\text{NO} + 200 \text{ ppb NO}_2$) and up to 30 hydrocarbons (50 ppb each). NO , NO_2 and O_3 are monitored in measuring cycles, including zero checks, by chemiluminescence analyzers (950A, 952A, Beckmann). Ozone levels are kept below 1 ppm by adding NO continuously at 1 ppb min^{-1} . The microcomputer collects and stores the data on light intensity, humidity, temperature and the concentrations of NO_x and O_3 . It also computes the dilution of the chamber contents (which is operated at ambient, atmospheric pressure) by

the gas consumption of the analyzers and aerosol samples.

The hydrocarbons, disappearing due to photochemical reactions, are monitored by capillary gas chromatography at 20 min intervals. An automatic cryogenic sample enrichment is used to achieve a detection limit of less than 1 ppb per component for hydrocarbons ranging from $\text{C}_2 - \text{C}_{16}$ from 20 ml samples /16,17/. Two gas chromatographs (Si-chromat, Siemens) are employed simultaneously, using an unpolar fused silica column (CP Sil 5, Chrompack) for universal detection of unpolar and polar compounds, and an adsorption column (Al_2O_3 PLOT, Chrompack), specific for hydrocarbons. Identification of products can be performed by applying long-path absorption (70 m) in a multiple-pass cell in the chamber in the spectral range from 10 - 40 000 cm^{-1} with an FT-IR/UV spectrometer (IFS 113v/IFS 85, Bruker), or by GC/FTIR or GC/MS (R-10-S, NERMAG).

The aerosols SiO_2 (Aerosil 200, Degussa, 200 $\text{m}^2 \text{g}^{-1}$), TiO_2 (PKP 09040, anatase, Bayer, 120 $\text{m}^2 \text{g}^{-1}$), Fe_2O_3 (Siccotram Orange, BASF, 150 $\text{m}^2 \text{g}^{-1}$), fly ash from a coal power plant (5 $\text{m}^2 \text{g}^{-1}$) and NaCl (Merck, p.a.) are used as model compounds for the atmospheric aerosol. For the simulation experiments, the aerosols are produced by an atomizing technique, using aqueous suspensions (or solutions in the case of NaCl) of the aerosol base materials and by drying the droplets to particles in a dry, highly purified air flow (containing less than 1 ppb/component of non-methane-hydrocarbons). The fly ash is dispersed by a dry, pulsed fluidized bed method. The aerosols are discharged by a ^{85}Kr β -radiation source prior to entering the chamber. Initial mass concentrations of 3 mg m^{-3} are reached at 0.5 μm mean particle diameter. Aerosol analysis /15,17-19/ is performed either by a laser straylight aerosol spectrometer (Royco 225), or by taking filter samples from a few dm^3 of air and determining the mass on a microbalance or the number and size by raster electron microscopy. In some experiments on models of the final chamber /19/, laser Doppler anemometry is used. A condensation nuclei counter, an electrostatic classifier, a diffusion battery, and a differential mobility analyzer are available for determining size distributions.

3 Results and Discussion

3.1 Aerosol Enclosure

Experiments on the decay rate of monodisperse aerosols made of

latex were performed in models (1:20, 1:10, 1:5) of the final chamber, using laser Doppler anemometry /19/. These experiments revealed that the major variables influencing the deposition of aerosols are the temperature gradient and the particle size. Since a spherical chamber (with an inherent minimum surface/volume ratio) appeared to be incompatible with the introduction of simulated sunlight and with simultaneous thermostating, we decided to use a cylindrical vessel with a thermostating of top and bottom, and with irradiation from the top. A minimum temperature gradient would optimize the residence times of the aerosols but prevent the gas content from mixing sufficiently rapidly. Hence, a small negative temperature gradient of -1 K m^{-1} was chosen as a compromise /15,19/. In the experiments, exponential decays of the aerosol mass density were always observed, defining a decay rate τ^{-1} . Figure 3 shows the dependence of the residence time on the aerosol particle diameter d in a double logarithmic diagram.

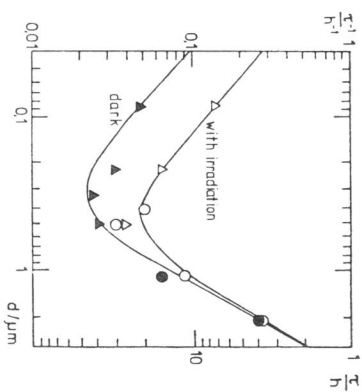


Fig. 3: Decay rate (left hand ordinate) and mean residence time (right hand ordinate) in dependence of aerosol particle diameter, determined from exponential decay curves of the number density of monodisperse latex aerosol. The vertical temperature gradient in the chamber was -1 K m^{-1} . The particle densities have been monitored by a laser stray-light aerosol spectrometer (triangles) and by electron microscopy of filter samples (circles).

At low diameter, the decay rate τ^{-1} increases inversely proportional with d . This behaviour is interpreted to be (approaching

molecular-) diffusion. At high particle diameter, the decay rate increases with d^2 , as expected for the sedimentation process (where the gravitational force, proportional to the mass $\sim d^3$, is balanced by the viscosity force, $\sim d$). A minimum decay rate is obtained at $0.5 \mu\text{m}$ aerodynamic diameter, corresponding to a residence time of 2 days in the dark and of 1 day in the presence of simulated sunlight. The decreased residence time in the presence of sunlight may be caused by increased turbulence (due to irradiation-heated cylinder walls), nevertheless the attained residence time enables us to perform experiments in the presence of aerosols over a period of several days, if sufficiently sensitive methods for aerosol analytics are available.

3.2 Quality Check of Gas Phase Analytics

In order to simulate environmental tropospheric conditions, a smog chamber technique should be applied at the ppb concentration level. The developed sample preconcentration method is able to analyze hydrocarbons and other organic trace gases qualitatively and quantitatively from 20 ml air samples down to the 1 ppb level at a high retention rate. Figure 4 shows an experiment on the dilution of the content of a 0.5 m^3 smog chamber by a constant flow of purified air. As expected for a well-mixed chamber, an exponential dilution at equal rates occurs for a range of hydrocarbons from propane to undecane, data being shown for several alkanes, alkenes and aromatics. In the simulation experiments on atmospheric degradation, NO_x is added to such mixtures, and upon irradiation with simulated sunlight OH , O_3 and other active species of the troposphere are formed. If NO is added continuously at a rate of 1 ppb min^{-1} , the reaction



limits the formation of O_3 to levels below 1 ppm.

Major sources of OH in smog chamber studies are contributed from heterogeneous reactions of NO_x with H_2O to form HONO , which is subsequently photolyzed:



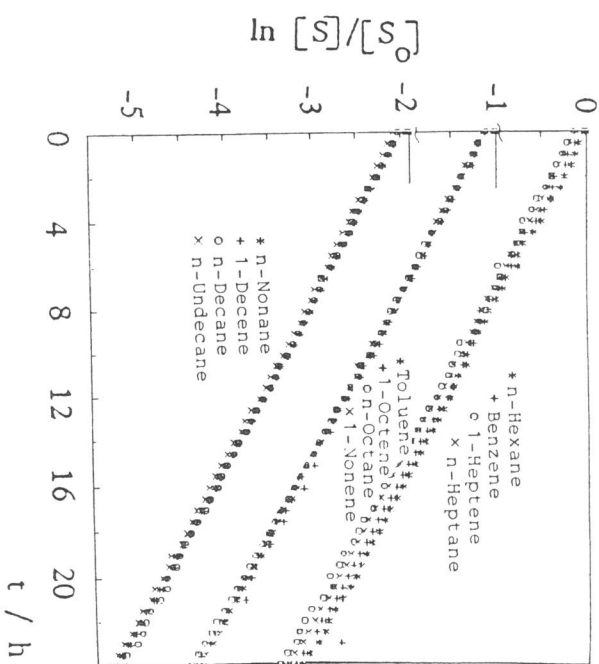


Fig. 4: Exponential dilution of smog chamber contents by a constant flow of diluting gas. The straight (and parallel) lines of the semilogarithmic diagram demonstrate the reproducibility of the sample preconcentration method and the absence of memory effects, which might be caused by wall adsorption. Initial concentrations are 50 ppb per component.

Further sources are photolysis of O_3 and subsequent reaction of $O(^1D)$ with H_2O



and regeneration of OH radicals from HO_2 or RO_2 (HO_2 and RO_2 are important intermediates in the atmospheric oxidation of organics) by the fast reactions



Since the alkanes are known to be rather inert against O_3 , their decay can be assumed to occur by reaction with OH alone, and figure 5 shows relative rate constants for the n-alkanes from propane to n-hexadecane, placed on an absolute basis by adjustment to the value recommended for n-decane /3/.

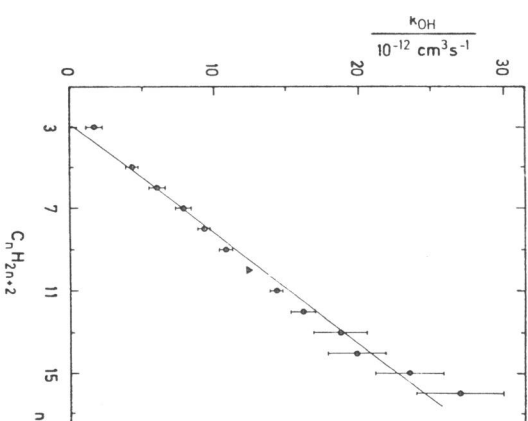


Fig. 5: Rate constants for the reaction of OH with n-alkanes from propane to n-hexadecane determined in a 500 l smog chamber at 312 K.

The observed rate constants increase linearly with the chain length of the n-alkanes, indicating a constant contribution for n-pentane to n-hexadecane of $1.6 \times 10^{-12} cm^3 s^{-1}$ per CH_2 group. The extension of the homologous series from hitherto investigated chain lengths of 10 C-atoms to chain lengths of 16 C-atoms demonstrates the applicability of our chamber to compounds with low volatility and high boiling point. Further rate constants for the reactions of OH radicals have been determined for a series of organics, listed in table I in comparison with recommended literature values. Similarly, rate constants for the reactions of several organics with O_3 have been determined by a competitive technique /17,20/. These rate constants are listed in table II compared to a recent literature review

Table I: Rate Constants, $k/10^{-12} \text{ cm}^3 \text{ s}^{-1}$, for the Reactions of OH with Various Organics at Room Temperature in Comparison with Values from a Review (Atkinson /3/)

Compound	This work	Lit.	Compound	This work	Lit.
Propane	1.3	1.18	2,2 Dimethylhexane	4.9	-
n-Butane	2.5	2.53	2,2,4 Trimethylpentane	3.4	3.66
n-Pentane	4.1	4.04	2,3,5 Trimethylhexane	7.9	-
n-Hexane	5.7	5.58	Cycloheptane	11.7	13.1
n-Heptane	7.3	7.2	Cyclooctane	14.1	-
n-Octane	8.8	8.72	1,1,3-Trimehyl-		
n-Nonane	10.3	10.0	cyclohexane	8.7	-
n-Decane	12.4	11.2	Adamantane	21.9	22.7
n-Undecane	13.3	-	Propene	28	26.3
n-Dodecane	13.9	-	Acrylonitrile	4.3	4.8
n-Tridecane	15.5	-	Propionitrile	0.8	0.19
i-Butane	2.5	2.37	Butyronitrile	1.1	-
i-Pentane	4.0	3.9	Benzene	1.3	1.28
3-Methylpentane	5.7	5.6	Toluene	5.6	6.19
4-Methylpentane	9.7	-	o-Xylene	10.3	14.7
2-Methylpentane	10.1	-	p-Xylene	11.6	15.2
2,3-Dimethylbutane	5.8	6.2	Chlorobenzene	1.0	0.7
2,3-Dimethylpentane	6.0	5.2	Vinyl Chloride	5.6	6.6
2,4-Dimethylhexane	7.8	-	1,1-Dichloroethene	7.0	-
2,2-Dimethylbutane	2.4	2.59	1,2-Dichloroethene	2.2	-
2,2 Dimethylpentane	3.4	-	Trichloroethene	2.2	2.36
3,3 Dimethylpentane	3.7	-	Carbon Tetrachloride	< 0.06	

/2/. The good agreement of our values with known values again is a quality test of the method; the error limits of the present study are superior to literature values. Numerous rate constants have been determined for the first time here, and this increased data base will improve the parameters, serving for predictions of rate constants for estimating the atmospheric lifetime of industrial emissions.

Table II: Rate Constants, $k/10^{-17} \text{ cm}^3 \text{ s}^{-1}$, for the Reactions of Ozone with Various Organics at Room Temperature in Comparison with Values from a Review (Atkinson and Carter /2/)

Compound	This work	Literature
Propene	1.1	1.13
i-Butene	1.3	1.21
1-Pentene	0.95	1.1
1-Hexene	1.1	1.17
1-Heptene	1.15	0.8-1.7
1-Octene	1.25	0.8
1-Nonene	1.45	-
Vinyl Chloride	0.014	0.017-0.2
Acrylonitrile	0.002	-
Propionitrile	<0.001	-
Butyronitrile	<0.001	-
o-Xylene	<0.007	7×10^{-5}
p-Xylene	<0.01	4×10^{-5}

3.3 Experiments in the Presence of Aerosols

3.3.1 SiO_2 Aerosol

From the decay rate of various hydrocarbons in the photochemog, the concentration time profile of OH radicals can be computed by using known rate constants for the reaction of OH. Experiments were performed to determine the influence of the aerosol presence on the concentration profile of OH. Figure 6 shows the behaviour of OH in the presence of SiO_2 aerosol and of TiO_2 aerosol at initial mass concentrations of 2 mg m^{-3} .

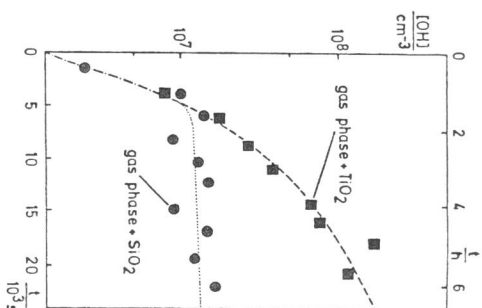
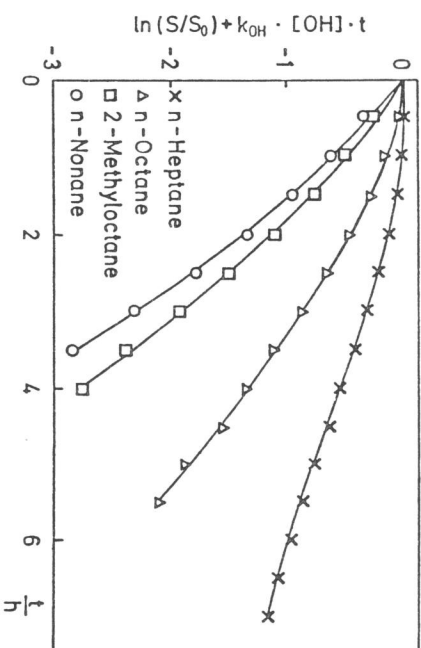


Fig. 6: Typical formation of OH in the aerosol smog chamber in the presence of SiO_2 or TiO_2 aerosol. In the absence of aerosol the formation of OH is similar to the curve observed in the presence of SiO_2 .

The uv-transparent SiO_2 aerosol is observed to have no significant influence on the time profile of OH, the curve being identical to the curve observed in the absence of aerosol. OH reaches a steady-state concentration of 10^7 cm^{-3} after 1 hour. The steady state is maintained for several hours. As mentioned above, it is known that OH is generated by heterogeneous removal of NO_x on wet surfaces to form HONO which is subsequently photolyzed. Although at 2 mg m^{-3} the total surface of the particles contributes 10^8 to the surface of the chamber and the particle density is of the order of 1 mm^{-3} , no influence of this readily available surface on the generation of OH is observed.

3.3.2 TiO_2 Aerosol

The concentration profile of OH in the presence of TiO_2 aerosol is included in figure 6 as well. After the primary establishment of the steady-state value of 10^7 cm^{-3} (observed in the absence and pre-



sence of SiO_2) the concentration increases further and exceeds a value of 10^8 cm^{-3} after a time period of 6 h. This increased concentration of OH is observed only in the presence of NO_x ; in the absence of NO_x ($< 3 \text{ ppb NO} + \text{NO}_2$), the values of the curve

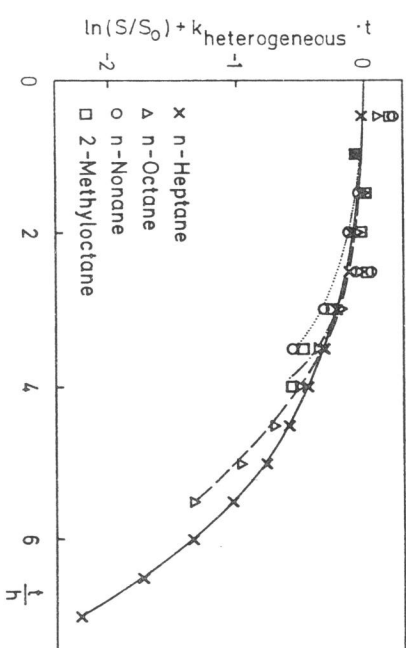


Fig. 7: Degradation of various hydrocarbons in the presence of TiO_2 aerosol. The lower figure shows the portion of the degradation by the well-known reaction with OH (determined from the decay of propane) in the gas phase. The upper figure shows the residual degradation, which is suggested to be a heterogeneous reaction, occurring on the surface of the photoactivated aerosol.

shown for SiO₂ aerosol are not exceeded. In addition, the decay rate pattern of the hydrocarbons is no longer in accord with consumption by OH. This is observed in a very pronounced manner if the concentration of NO_x is kept low enough (< 3 ppb). Figure 7 shows the decays of n-heptane, n-octane, 2-methyloctane, and n-nonane, divided into two portions.

The portion for the well-known homogeneous gas phase reaction is determined by assuming that propane (not included in the figure) is consumed by reaction with OH alone. The decays, observed for n-heptane through n-nonane (lower figure), exhibit only a slight acceleration, as expected for the only gradual increase from 5 to 7 CH₂ groups contributing to the reaction with OH. The remaining decay (upper figure) exhibits a very pronounced increase with the chain length (the decay is increasing not linearly but exponentially with chain length). Table III contains some rate data on this (obviously heterogeneous) process. The relative efficiency of this process increases with decreasing humidity, as can be seen for the long-chain alkanes and for the aromatics, the effect being most pronounced for the xylenes. The dependence of this photodegradation on the humidity and on the volatility of the compounds is a strong hint at a heterogeneous process, occurring on the surface of the photoactivated TiO₂ aerosols.

Table III: Heterogeneous Photodegradation of Organic Compounds (Relative to n-Heptane) in the Presence of TiO₂ at Three Relative Humidities

Compound	~ 70% R.H.	25% R.H.	< 5% R.H.
n-Butane	0.05	0.07	-
n-Pentane	0.14	-	0.11
n-Hexane	0.38	0.32	-
n-Heptane*	1	1	1
n-Octane	2.6	2.9	2.7
n-Nonane	6.2	7.7	10.4
Cyclohexane	-	-	0.29
Cycloheptane	1.8	1.1	0.92
Cyclooctane	4.2	2.5	2.6
Benzene	0.26	0.51	0.53
Toluene	2.2	4.5	9.5
Ethylbenzene	8.0	-	26.2
o-Xylene	10.1	26.6	95
p-Xylene	10.2	35.5	> 100
Chlorobenzene	0.8	1.6	1.7
o-Dichlorobenzene	-	-	4.5
p-Dichlorobenzene	-	-	3.5

*: Reference Compound

Figure 8 shows the dependence of the heterogeneous photodegradation on the vapour pressure of the compounds in a logarithmic diagram.

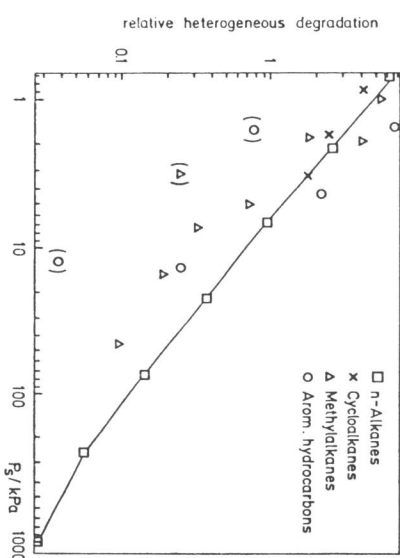


Fig. 8: Heterogeneous photodegradation (relative to n-heptane) of various organic compounds in dependence on the saturated vapour pressure at 29°C. Outliers in the correlation (the slope of the line drawn through the n-alkanes indicates inverse proportional behaviour) are represented in brackets.

The data for the n-alkanes demonstrate an inverse proportionality between photodegradation and vapour pressure over almost 3 orders of magnitude. For an extreme example, a monolayer of di(2-ethylhexyl)-phthalate, permanently adsorbed on the TiO₂ aerosol, disappeared by more than one order of magnitude faster than p-xylene at 70% relative humidity. The dependence on vapour pressure is supported by the data for the branched-chain alkanes, the cycloalkanes and the aromatics, although the scatter is considerably larger. Extreme outliers in the diagram are represented in brackets: 2,2,3,3-tetraethylbutane is an almost spherically shaped branched-chain paraffin with a low tendency towards adsorption, chlorobenzene (upper left) is a deactivated, halogenated aromatic, hexafluorobenzene (bottom) even a perhalogenated aromatic. The heterogeneous nature of the degradation is supported by the higher degradability of the (with respect to benzene) less volatile chlorobenzene. If adsorption times can be correlated with the degradability, the data might be compared with retention times of the compounds on a chromatographic adsorption column, as shown in Fig. 9.

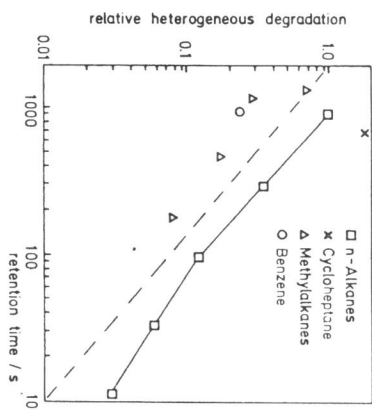


Fig. 9: Correlation of the heterogeneous photodegradation with retention times, determined on a packed TiO_2 column at room temperature.

The correlation is not improved, and regrettably the retention times of the higher alkanes and aromatics are too long to be determined precisely. On the other hand, by analogy with the well-known behaviour of Al_2O_3 adsorption GC-columns, the retention times of which show a marked dependence on humidity (at high humidity the retention times are decreased). The same behaviour can be expected for the mean time of adsorption. A similar behaviour can be expected for the rate of the heterogeneous photodegradation listed in table III.

Using the Langmuir theory, the mean time for adsorption, τ , of a molecule on the surface can be estimated from the equation

$$\tau = \tau_0 \exp(Q_{\text{ads}}/RT), \quad (7)$$

where τ_0 is approximated by 10^{-13} s, and Q_{ads} in the Boltzmann-factor is the heat of adsorption (the smaller heat of vapourization, taken from the vapour pressure curve, may be used for a model as a first estimate). From equation 7 the mean times of adsorption can be estimated to be of the order of 10^{-8} s for n-pentane and 10^{-5} s for n-nonane, a time sufficient for the reaction of the compounds in the adsorbed state.

The photoactivity of TiO_2 , a well-known n-type semiconductor material, may be explained from the following reactions:



where the photoactivated aerosol photoadsorbs O_2 from the air by means of the photoelectrons. The photoadsorbed O_2^- is in pH-dependent equilibrium with HO_2 , involving H^+ from the water layer to form HO_2 . The positively charged sites (defect electrons) may then react with OH^- from the water layer to form OH . These active species on the surface of the photoactivated semiconductor aerosol may oxidize adsorbed compounds.

The importance of this process for the chemistry of the atmosphere will depend on the density and photoactivity of environmental aerosols. Evidence for a ranking of increasing photoactivity exists for SiO_2 , Al_2O_3 , SnO_2 , MgO , coal fly ash, Fe_2O_3 , sea sand, TiO_2 (anatase), ZnO and TiO_2 (rutile) from experiments on the degradation of an adsorbed layer (less than a monolayer) of phenanthrene on these materials in a rotating drum photoreactor, using a fluorescent lamp light source /21/. On the other hand, another type of coal fly ash was observed to be even less active than SiO_2 (silica gel) /21/. It should be noted that the photoactivity of TiO_2 aerosol occurred even in the absence of uv, at $\lambda > 360$ nm, using an acrylic glass cut-off filter between the chamber and the solar simulator. Hence, the photoactivation of aerosols may still occur on hazy days or in the winter season, when production of OH in the gas phase has almost ceased, due to atmospheric light scattering.

3.3.3. Fe_2O_3 Aerosol and Coal Fly Ash

Experiments were also performed in the presence of Fe_2O_3 aerosol and coal fly ash. The formation of OH remained unaffected in the presence of these aerosols within the reproducibility of about 50%. The rate constants for the reactions of OH with various compounds (similar to those investigated in the presence of TiO_2) remained unchanged in the presence of Fe_2O_3 and fly ash, with the exception of some aromatics in the presence of Fe_2O_3 . Fig. 10 shows

data for *o*- and *p*-xylene and ethylbenzene for an additional photodegradation, which is too weak to be detected with benzene and other hydrocarbons.

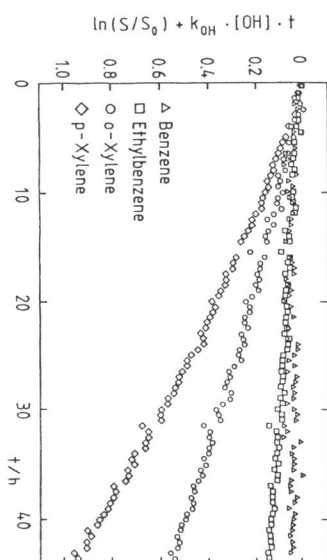


Fig. 10: Portion of the decay of aromatics in the presence of Fe_2O_3 aerosol that is not caused by reaction with OH in the homogeneous gas phase. The decay depicted in the figure is interpreted to be due to a heterogeneous photodegradation.

The degradation process is slow, 30% of *p*-xylene are left even after 40 h. This photodegradation could only be detected by suppressing the formation of OH (by using the acrylic glass uv cut-off filter for 360 nm). On the other hand, Fe_2O_3 is a more prominent aerosol constituent in the environment than TiO_2 , and the effect can be expected to increase with decreasing vapour pressure of the compounds. For instance, polycyclic aromatics might be affected by such a process very efficiently (considering their almost infinite residence time in the adsorbed state) compared to *p*-xylene with only 10^{-5} s. The wavelength dependence of the photoactivity should be checked with various iron oxide-containing aerosols; other fly ashes should be checked as well, since the reactivity of fly ash is known to vary considerably. Mineral dusts and sands with their yellowish colour absorb light in the visible, which might trigger heterogeneous photooxidation of adsorbed compounds. Whether the oxidation mechanism of Fe_2O_3 is similar to the behaviour of TiO_2 could not be checked because of the low observed reactivity of Fe_2O_3 . On the other hand, it should be noted that heterogeneous photodegra-

dation of a monolayer of di(2-ethylhexyl)phthalate, a widespread plasticiser, was observed at a half-life of a few hours, when the uv cut-off filter was removed. This is a similarity to TiO_2 , where a half-life of less than 20 min was observed.

3.3.4 NaCl Aerosol

Sodium chloride aerosol was chosen as a model for sea spray, which is the aerosol with the largest source strength. In the presence of NaCl aerosol the decay of the hydrocarbons was observed to be in disagreement with known rate constants of OH (especially the alkanes disappeared by far too quickly compared to the aromatics). Fig. 11 shows a typical smog chamber run, where the observed decay has been split into two portions; the well-known consumption by OH in the gas phase (lower figure) and the unknown process (upper figure).

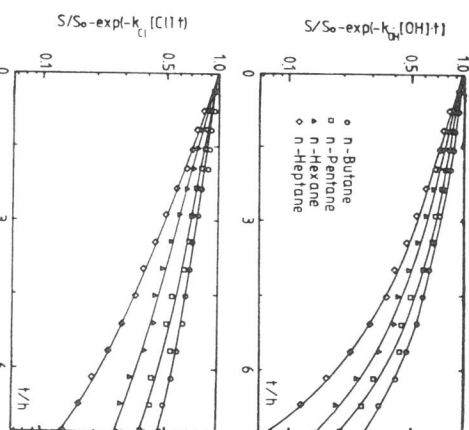


Fig. 11: Degradation of *n*-alkanes in the presence of NaCl aerosol.

The lower figure shows the portion due to OH radicals, the upper figure the portion due to Cl atoms. The corresponding concentrations of OH and Cl have been computed from the decay rate pattern of various aromatics and alkanes, where toluene is a major indicator for OH and 2,2,3,3-tetraethylbutane for Cl (see also figure 12).

Since the consumption increases linearly with chain length, not a heterogeneous but a homogeneous gas phase reaction is presumed to occur. The most reasonable assumption is that the species responsible for the unknown consumption process is atomic Cl.

This assumption was proven to be true by checking several compounds with known rate constants for reaction with both Cl and OH. Similar decay properties of the hydrocarbons could be achieved, when Cl atoms were produced by photolyzing Cl₂. In addition, the same behaviour could be observed by adding chlorinated hydrocarbons (trichloroethene, chlorobenzene and others). The ratio of [OH]/[Cl] during such smog chamber runs was observed to vary between 100 (at the beginning) and 10 at the end of several runs. Rate constants for the reaction of Cl, determined by the various techniques are listed in table IV. The comparison with recent literature values /22/ yields excellent agreement.

Table IV: Rate Constants, $k/10^{-10} \text{ cm}^3 \text{ s}^{-1}$, for the Reactions of Cl Atoms with Various Organics, in Comparison with a Recent Study by Atkinson and Aschmann /22/. Sources of Cl: NaCl Aerosol in Photosmog (I), Photolysis of Cl₂ (II), Photodegradation of Chlorobenzene, Vinyl Chloride, Trichloroethene and 1,1-Dichloroethene (III)

Compound	I	II	III	Literature
Propene	1.09	-	1.02	1.34
n-Butane*	1.97	1.97	1.97	1.97
n-Pentane	2.65	2.30	2.35	2.52
n-Hexane	3.15	3.00	3.20	3.03
n-Octane	4.25	3.65	-	-
n-Nonane	4.40	-	-	-
i-Butane	1.35	-	1.30	1.37
1-Pentane	2.10	-	1.75	2.03
3-Methylpentane	2.70	-	2.80	-
2,2-Dimethylbutane	1.60	1.75	-	-
2,3-Dimethylpentan	3.00	-	-	-
2,2,4-Trimethylpentane	3.30	-	-	-
2,2,4-Trimethylhexane	2.25	2.25	-	-
2,2,3,3-Tetramethylbutane	2.25	1.55	-	-
Propene	-	-	-	2.44
Vinyl Chloride	3	-	1.90	1.97
1,1-Dichloroethene	2.05	1.55	-	-
Benzene	2.10	-	-	0.15
Toluene	0.05	-	-	-
	0.74	0.66	-	0.589

*: Reference Compound

The environmental relevance of such a contribution of Cl-atoms compared to OH radicals might be considerable, although the reactions, leading to such high concentrations of Cl and regenerating Cl from the rapidly formed HCl, are mostly unknown. The book by Graedel /1/ quotes a figure of $2 \times 10^4 \text{ cm}^{-3}$ for the concentration of Cl in the troposphere without giving a detailed reference. The following figure 12 demonstrates the consequences of such a scenario, where rate constants for the reactions of hydrocarbons and chlorocarbons are depicted in a double logarithmic diagram.

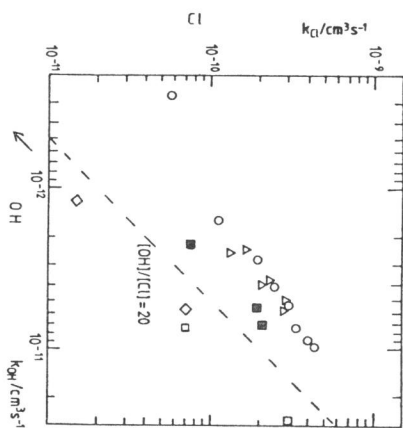


Fig. 12: Cl- and OH-reactivities of various n-alkanes (O), branched-chain alkanes (Δ), alkenes (\square), chloroalkanes (\blacksquare) and aromatics (\diamond). The arrow points in the direction, where methane is situated. The line divides the figure into two regions, where Cl (upper left) and OH (lower right) respectively are expected to dominate tropospheric degradation, if $[\text{OH}]/[\text{Cl}] = 20$.

The line divides the compounds into two groups: where consumption by OH is dominating (lower right), and where Cl is dominating (upper left). The figure shows that under the assumption that $[\text{OH}]/[\text{Cl}] = 20$ in the troposphere the decay of only CH₄, benzene, toluene, ethene and propene would be governed by OH, all other compounds with known rate constants with Cl and OH are consumed predominantly by Cl, with ethane being the most sensitive indicator for Cl.

This (still highly speculative) assumption can get further support by an attempt to determine OH from the relative degradation of various aliphatics in the plume of the Ruhr-area. Figure 13 on the left shows a plot of the decay rate of various aliphatics divided by the respective rate constants with OH, taking the concentration of C_2H_2 as an almost inert-tracer /23/.

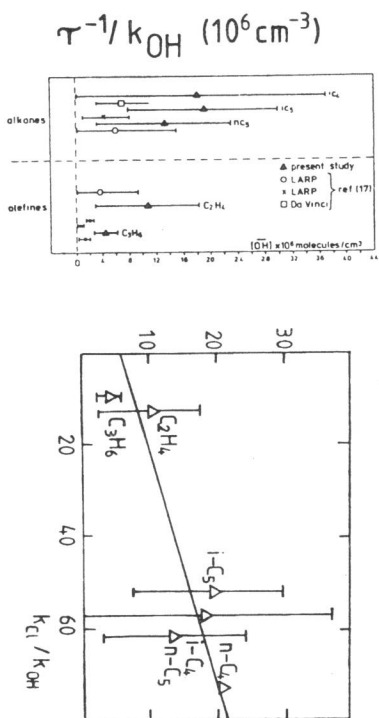


Fig. 13: Tropospheric degradation of various alkenes and alkanes relative to C_2H_2 in the plume of the Ruhr-area. The left-hand figure is taken from a paper by Neuber et al. /23/, the right-hand figure presents a reinterpretation of the data, considering the reactivities of the compounds against Cl. The straight line is an estimate for $[OH]/[Cl] = 20$, yielding a more reasonable value for $[OH]$ of $6 \times 10^6 \text{ cm}^{-3}$, and $3 \times 10^5 \text{ cm}^{-3}$ for $[Cl]$. Thus the previously /23/ observed discrepancy for the alkanes can be solved.

The figure shows an obvious discrepancy between the alkenes and the alkanes, which has been similarly observed by other authors.

If the contribution of Cl to the decay of the hydrocarbons is considered, the total decay rate can be described by the equation

$$\tau^{-1} = k_{OH} [OH] + k_{Cl} [Cl] \quad (13)$$

By dividing this equation by k_{OH} , the expression

$$\tau^{-1}/k_{-H} = [OH] + [Cl] k_{Cl}/k_{OH} \quad (14)$$

is obtained. Hence, a plot of τ^{-1}/k_{OH} versus the ratio k_{Cl}/k_{OH} should yield the concentration of OH as intercept and the concentration of Cl as slope. The straight line yields values of $6 \times 10^6 \text{ cm}^{-3}$ for $[OH]$ and $3 \times 10^5 \text{ cm}^{-3}$ for $[Cl]$, if a ratio of 20 for $[OH]/[Cl]$ is supposed. Although the error limits of the decays are not sufficiently low to give strong support to this procedure, the discrepancy between the alkenes and alkanes is solved properly. On the other hand, it should be noted that any other chemical process - removing alkanes (or less volatile compounds) predominantly - would solve the discrepancy as well. Further work on the sources of Cl atoms in tropospheric chemistry from degradation of chlorocarbons and NaCl aerosol is in progress.

Acknowledgement

This work was supported by the Bundesminister für Forschung und Technologie and by the Verband der Chemischen Industrie (Companies BASF, Bayer, Henkel, Hoechst and Hüls). The author thanks his co-workers Dr. W. Behnke, Dr. F. Nolting, K. Dziobek, M. Elend, H.-U. Krüger, and J. Zorn. Helpful discussions with Prof. W. Stöber and the members of the Steuerungsgruppe Photoabbau are gratefully acknowledged.

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Monographien

Sammelbände mit
Einzeldarstellungen über
Forschung und Entwicklung auf
Gebieten des
Chemischen Apparatewesens,
der Chemischen Technik und
der Biotechnologie

begründet von
Max Buchner† und Herbert Bretschneider†
herausgegeben im Auftrag der DECHEMA
von Dieter Behrens

DECHEMA
Deutsche Gesellschaft für Chemisches Apparatewesen,
Chemische Technik und Biotechnologie e.V.
Frankfurt am Main



Monographs vol. 104
Formation, Distribution and Chemical
Transformation of Air Pollutants

Formation, Distribution and Chemical Transformation of Air Pollutants

Papers of the
Workshop held in Frankfurt am Main,
5 to 6 February 1986
Edited by R. Zellner



DECHEMA
Deutsche Gesellschaft für Chemisches Apparatewesen,
Chemische Technik und Biotechnologie e.V.
Postfach 97 01 46, Theodor-Heuss-Allee 25, D-6000 Frankfurt 97

CIP-Kurztitelaufnahme der Deutschen Bibliothek

Formation, distribution and chemical transformation of air pollutants: papers of the workshop, held at Frankfurt am Main, 5 to 6 February 1986 / (DECHEMA, Dt. Ges. für Chem. Apparatewesen, Chem. Technik u. Biotechnologie e.V.). Ed. by R. Zellner. — Weinheim: New York: VCH, 1987

(DECHEMA monographs: Vol. 104)

ISBN 3-527-10991-9

NE: Zellner, Reinhard (Hrsg.); Deutsche Gesellschaft für Chemisches Apparatewesen, Chemische Technik und Biotechnologie;
DECHEMA-Monographien

Vertrieb an Nicht-Dechema-Mitglieder:

VCH Verlagsgesellschaft, Postfach 1260/1280, D-6940 Weinheim

(Federal Republic of Germany)

USA und Canada: VCH Publishers, 303 N.W. 12th Avenue, Deerfield Beach Fl 33442-1705 (USA)

Herausgegeben von R. Zellner, Göttingen

in Zusammenarbeit mit der

DECHEMA Deutsche Gesellschaft für Chemisches Apparatewesen,

Chemische Technik und Biotechnologie e.V., Frankfurt am Main

Umschlaggestaltung: Weisbrod-Werbung, Birkenau

Redaktionelle Bearbeitung: Wolf-Heinrich Kühne, Frankfurt am Main

Verantwortlich für den Inhalt: Die Verfasser der Beiträge

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Reihe Dechema Monographien ISSN 0070 315

Band 104 ISBN 3-527-10991-9

Gesamtherstellung: Schön & Wetzel GmbH, Frankfurt am Main

Printed in Germany

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Preface

It is one of the fundamental laws of nature that the application of man-made technology, but even human living itself, must be associated with environmental pollution. The pollution of air in urban areas has been recognized for centuries and its adverse effect on human health is well documented. With the beginning of industrialization at the end of last century we have seen a dramatic increase of anthropogenic emissions and a spread of air pollution both in extent and dimension. Although local and regional effects are still primary concerns of air pollution there is now also a strong global component with a focus on future habitability of our planet.

Anthropogenic emissions into the air and their environmental consequences remain to be a challenge to science and technology. We are facing a multi-layered problem with the

- i) formation of pollutants and their reduction by optimized process technology
- ii) distribution and chemical transformation of pollutants
- iii) changes of the quality of air and precipitation and their effects on the biosphere
- iv) changes in global trace gas composition and climate

as key elements. The scientific and technological statements are consequently very complex and advances can only be expected by interdisciplinary endeavours of engineers, chemists, meteorologists, and biologists.

To set the stage of only a few aspects: Quality and quantity of anthropogenic emissions can easily be determined from consumption figures or production patterns. It is more difficult to quantify their contributions relative to natural emissions and, finally, it is an unresolved problem how observed changes in the biosphere can be related to anthropogenic emissions. This is not surprising since even for clean air sources, sinks, and chemistry of its reactive components are not sufficiently characterized.

The entire subject of air pollution cannot be covered by a single symposium. The present workshop has focussed on a number of chemical aspects of the formation distribution and transformation of air pollutants. The latter is mainly and conventionally the chemistry of the homogeneous gas phase. However, the presence of aerosols in the lower troposphere also requires the inclusion of heterogeneous chemical and photochemical processes. Although perhaps not as far advanced in knowledge these heterogeneous aspects of air pollution chemistry appear to deserve equal attention.

The workshop was organized by DECHEMA under the auspices of the committees "Abgase" and "Gas und Flammenreaktionen". The following have contributed gratefully to the preparation and realization of the workshop: Prof. Dr. D. Behrens, Mrs. C. Birkenberg, Prof. Dr. K. Kirchner, Dr. K. Trobisch, Prof. Dr. H. Gg. Wagner, and Dr. J. Wiesner. The editorial details of this monograph were in the hands of Mr. W. H. Kühne and his coworkers. To all of them our thanks!

R. Zellner, Göttingen, June 1987

Air: Breath of Life and Object of Study

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Development and Information, Leverkusen

It is a remarkable development, indeed, to see that an essential part of our world, which for millennia was never the object of curiosity, let alone research, is now in the focus of science, legislation and politics; a part of our world that for centuries was used only to drive our first sailing boats and our last windmills.

Air has become an object of public interest.

We felt we were through with air

- when Torricelli invented the mercury barometer and proved that air is physical matter, that it has mass and exerts pressure, and
- when Lavoisier proved, via mercury - mercuric oxide transformation, that air is a mixture of gases, of which one sustains a fire, while the other does not - or the others do not, as was said later, when it was discovered that, besides nitrogen, carbon dioxide and the rare gases also make up the other part.

The role of oxygen became clear in both directions when the major global cycles in nature were perceived

- consumption by respiration and biological decay
- formation by photosynthesis.

Finally, Warburg seemed to settle the issue by clarifying the role of chlorophyll, finding that 4 photons with a wavelength of 660 nanometers are required per molecule of carbon dioxide, corresponding to 725 kJ/mol CO₂.

Thus, air passed out of the scope of the chemist as an object of interest and investigation; it had meanwhile become the center of aerodynamics and fluid mechanics; air nowadays seems to be the domain of aviation engineers and physicists. Meteorologists deal with it too, and on television the complete weather chart with isobars and forecasts appears on Saturday evening, just before the lottery figures.

Air as an environmental compartment, as essential for life, was more felt than understood

- the ancient Greeks spoke of pneumonia
- Genesis uses clay and breath to create Adam
- we speak of air to breathe as an undisputed minimum.

Occasionally, air pollution was also mentioned

- mal-aria, bad, sick-making air from the swamps; that it was a mosquito having its breeding grounds there, was discovered later
- "non licet aerem corrumpere" was written by Trebonius into the Codex Aureus
- late medieval London prohibited the use of coal in open fireplaces; wood or charcoal did not produce evil-smelling smoke.

In more sober words, we today speak of air as an object of scientific investigation and protection, as an environmental compartment comprising a number of functions.

Air is

- a container for natural and anthropogenic emissions, such as gases, dusts, solid-liquid aerosols and particle-bound substances of many kinds
- a vehicle to transport all these from land to sea and vice-versa, depending on the hemisphere, depending on the season
- a reactor, where chemical reactions take place, transformations and degradations, particularly when the sun supplies the necessary energy for activation.

The latter is essentially the subject of this symposium.

Remarkably, we see that the tools for experimental work were made available almost at the same time as the feeling for a necessity to look into that type of problem arose: they were improved and became more sophisticated as research progressed, although funds were often rather tight.

Almost the same goes for the investigations of conditions and processes prevailing in the atmosphere carried out at university level - there are nowadays national and international programs, some in cooperation with industry - as well as for practical developments in different sectors of technology.

The latter mainly involve process engineering work with the aim of controlling air pollution by

- purification of exhaust gas from chemical processes
- purification of flue gas from combustion processes of various types
- process changes and redesigns to reduce exhaust gas a priori in order to have lesser amounts or smaller concentrations for subsequent exhaust gas purification.

For the outsider, there are some well-known markers, publicized in the media and elsewhere

- the smog of Los Angeles
- the blue sky over the Ruhr Valley
- forest damage and acid rain
- the Cat-Car with catalytic conversion of automobile exhausts.

To the insider, the whole thing looks less exciting; more like a chain of events, an as yet unfinished series of diligently performed step-wise projects - the usual course in science - a continuous succession of work and results, whose success is far more evident in retrospect than when looking forward; this is particularly true when looking at applied technology in industry.

Nevertheless - despite this continuous work, and perhaps particularly then, since inherent pauses are lacking - it seems advisable to stop from time to time, to review the situation and to repeat the old questions

- what have we done so far?
- what follows from that?
- what should be done in the future?

I have no doubt that substantial contributions will be presented today and tomorrow in relation to questions 1 and 2, and we certainly can expect suggestions and proposals on question 3.

I'd like to comment on that particular question right at the beginning of this symposium, for I feel that an essential aspect of "what should be done in the future" could otherwise be overlooked.

We should make clear what has been done and what the meaning and impact of this work has been. In the long run, to all of our fellow citizens, and even more so to those who speak in their names as elected members of our community, with a mandate to enact laws and ordinances, and to implement administration.

In a short run, we should make all of this clear to our own colleagues in the scientific community, in the very widespread field of research in general; they too ought to know what has been achieved in this particular subject. Scientific progress can be very fast

in sectors - that is one part of the problem, we could call it the scalar component. However, there is also a vector in scientific progress: We in the scientific community are, by working in our particular fields of study, actually diverging from each other; we are beginning to have trouble in understanding each other's progress.

Some things which started as research in a niche stay that way, perhaps for quite a time, while others, having surpassed a certain level of insight gain an impact in a general scientific context, acquire a fundamental meaning in the mosaic of this world.

I feel atmospheric photochemistry has reached this level. The findings ought to be presented, at least in general terms and with a few figures. One should be able to say that there has been an enormous reactor in the sky ever since the atmosphere has contained oxygen and water, that an essentially stationary concentration of OH radicals and ozone takes care of oxidative degradation of substances, that, regardless of type and structure, nearly all substances are degraded with a speed, the reaction constant of which lies within two orders of magnitude, regardless of natural or anthropogenic origin. This is in simplified terms as far as you can go today in order to transmit the message in principle.

The photochemistry of the atmosphere is no longer in a niche no outsider enters for fear of getting lost. Photochemistry has come out.

Please help it to be seen in its full dimensions; after all, light is one of our tools.

The Oxidative Potential of the Troposphere and Its Influence by Hydrocarbon Emissions

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Summary

The earth's atmosphere is a giant photochemical reactor in which sun light produces highly reactive oxidants, notably OH radicals. Despite their extremely small concentrations (10^{-5} - $3 \cdot 10^{-6}$ molecules/cm³ for the day time troposphere) OH radicals essentially initiate all chemical transformation and therefore represent the oxidative potential. OH is formed by O₃ photolysis in the presence of H₂O vapour. Together with HO₂ the OH radical participates in a rapid cyclic HO_x transformation which is driven by CO and NO and terminated by HO_x recombination reactions. Using a simple photochemical box model it is shown that the steady state OH concentration is lower in the clean troposphere than in polluted continental air. This effect is amplified in the presence of hydrocarbons which in their oxidation chains consume (low NO) or produce (high NO) net HO_x.

Zusammenfassung

Die Erdatmosphäre ist ein riesiger photochemischer Reaktor, in dem das Sonnenlicht hochreaktive Oxidantien, wie das OH-Radikal, erzeugt. Trotz seiner extrem niedrigen Konzentration (10^{-5} - $3 \cdot 10^{-6}$ Moleküle/cm³) wird nahezu jegliche chemische Transformation durch das OH-Radikal eingeleitet. Es repräsentiert deshalb das oxidierende Potential. OH wird gebildet durch O₃-Photolyse in Gegenwart von Wasserdampf. Gemeinsam mit