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Degradation of Benzene in the Environment[1]

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Knowledge of the degradation of any chemical in the environment is important for different aspects:

—the degradability contributes to the estimation of the exposure both for men and the environment,

—the knowledge of degradation pathways, additionally, gives indications concerning the potential exposure to degradation intermediates,

—the overall degradation in the environment shows the potential of its biotic and abiotic compartments for eliminating a chemical or leading it into natural cycles.

Degradation, however, is only one of the important parameters (shown in Fig. 1) contributing to the assessment of exposure probability, and thus the probability of becoming effective in men or other organisms (*1*).

For an introduction to the topic, we would like to briefly discuss benzene in comparison to other chemicals regarding some of these parameters. A chemical which is produced and used only in very low quantities is most unlikely to result in problems in the general environment. In any case, effects are related to the level of exposure if the concept of threshold levels is accepted. Benzene, as a major base chemical, has a global annual production of 14 million tons. It is, thus, in the range of 10% of the total annual global production of organic chemicals (Table 1).

Following its use pattern, only a part of this production, however, has uses which can result in a significant release into the environment. The sources of benzene in the environment have been well defined, and there are a great number of data on its occurrence. Following the analytical feasibility, these data are mainly restricted to the occurrence in the atmosphere and the hydrosphere.

Table 2 shows some data of benzene and alkyl benzenes in the air. These concentrations are mainly due to traffic; e.g., the 69 $\mu g/m^3$ given for Berlin in November 1976 was found in a street with heavy traffic and is a mean value. There are daily and seasonal fluctuations resulting in a fluctuation over a year between 7 and 193 $\mu g/m^3$ (*2*).

Although not as many data are available for the occurrence of benzene in water, it has been well established that it may occur in surface water, ground water, and

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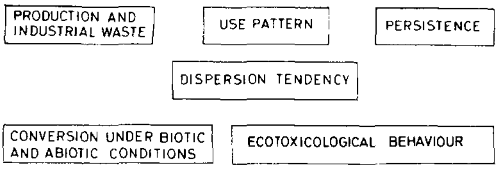

FIG. 1. Parameters determining the ecotoxicological potential of chemicals.

even drinking water. The concentrations shown in Table 3 are in the range of nanograms per liter (*3*).

In the recent survey on organic micro pollutions in water published by the European Communities and including several thousands of chemicals, benzene is mentioned only twice for surface and tap water, again in concentrations of nanograms per liter.

Although in this paper major emphasis is given to benzene in the general environment, it should be mentioned that it also occurs in enclosed environments (*4*).

Table 4 shows the chemicals which have been identified in the air of spacecrafts. This is admittedly a special environment; nevertheless the occurrence of a number of chemicals in the air of spacecrafts is indicative of their presence in technologically well-equipped environments.

One additional important question for the prospective evaluation of a chemical is the estimation of the trend of exposure. Is the occurrence in the environment constant, decreasing, or increasing? The level of occurrence is caused both by the amounts released and, on the other hand, by the amounts eliminated from the environment.

Anticipating a 2% increase in production and under the assumption that the portion of the produced chemical which is released into the environment remains constant 100 years from now, the concentrations in the environment could be 700-fold those which we have today (Fig. 2). This would mean that we would have roughly levels in mg/m^3 which are today in μg/m^3, and for biologically active chemicals there would be no question of significant harm.

TABLE 1

SELECTION OF CHEMICALS WITH ANNUAL GLOBAL PRODUCTION > 50,000 TONS (COMPILED FOR OECD BY GERMAN AD HOC GROUP)

Oganics	1,000 tons	Inorganics	1,000 tons
Acetaldehyde	2,400	Aluminium oxide	17,000
Acrylonitrile	2,700	Ammonia	40,000
Alkylbenzenes	700	Chlorine	24,600
Benzene	14,400	Iron sulfate	450
Carbon tetrachloride	1,000	Lead oxides	363
Chloroparaffins	270	Nitric acid	23,000
Cyclohexane	2,800	Phosphoric acid	13,000
Dibutyl phthalate	230	Sodium chlorate	600
Phthalic acid anhydride	2,300	Sodium chromate	
Toluene	8,500	+ bichromate	450
Trichloroethylene	700	Sulfuric acid	108,300
Vinyl chloride	7,730	Zinc oxide	420

TABLE 2

CONCENTRATIONS OF AROMATIC HYDROCARBONS IN AIR ($\mu g/m^3$)

	Los Angeles 1966	Toronto (1971)	Rotterdam (tunnel) 1974	Pretoria 1975/1976	Berlin Nov. 1976
Benzene	52	45	87	20	69
Toluene	152	123	156	36	147
m-*p*-Xylene	102	—	125	19	100

Therefore one approach for predictive evaluation is to assess the degradability of the respective chemicals in the environment and the degradation capacity of the relevent compartments of the environment.

Available evidence shows that the major route of benzene into the environment is emission into the air. Thus the fate in the atmosphere seems to be of primary importance. Before discussing this, some information should be given on biotic changes.

Biotic Degradation

The degradation of benzene, a base chemical of major importance, has been thoroughly investigated in a number of organisms. Degradation in this context means the metabolic alteration of the chemical structure and not necessarily the final breakdown to carbon dioxide. Many reviews have been published on the metabolic pathways of benzene in a variety of organisms from men to microorganisms. The available knowledge in this area includes the overall quantitative metabolic patterns as well as the different routes of decomposition to muconic acid

TABLE 3

ORGANIC CHEMICALS IN WATER (μg/liter; ppt)

	Lake of Zürich				
Compound	Suface	30-m Depth	Well water	Ground water	Tap water
Benzene	28	22	18	45	36
Trichloroethylene	38	65	5	80	105
Tetrachloroethylene	140	420	12	1850	2100
Chlorobenzene	3	12	—	14	6
Dichlorobenzene	16	26	—	—	4
Trichlorobenzene	6	42	—	—	4
Camphor	12	2	2	—	2
Naphthalene	8	52	—	—	8
Pentadecane	16	4	2	2	4
Heptadecane	20	4	1	—	3
Diphenylether	48	8	—	3	3
Tributylphosphate	82	54	—	10	14
Gasoline	~2000	~100	~50	~800	~800

(Grob, 1974)

TABLE 4

BENZENE IN ENCLOSED ENVIRONMENTS

Compound	mg/m^3
Methanol	0.0002
Ethanol	0.1
Isopropanol	0.14
n-Butanol	0.025
Isoprene	0.028
Benzene	0.018
Toluene	0.11
n-Hexane	0.004
Cyclohexane	0.0012
n-Octane	0.024
Octene-2	0.13
Mesitylene	0.0095
Xylenes	0.064
Ethyl benzene	0.011
Acetone	0.024
Methyl acetate	0.0014
Ethyl acetate	0.069
Isopropyl acetate	0.06
Methyl chloroform	0.13
Trichloroethylene	1.04
Tetrachloroethylene	0.16
Chloroform	0.001
Dichloroethane	0.011
Carbon tetrachloride	0.0019

and others and the distribution of the important metabolites in different organs. These data are most important for the toxicological evaluation and are of high scientific interest to improve the knowledge on the routes of chemicals in organisms. These important investigations, however, do not allow estimation of the degradation

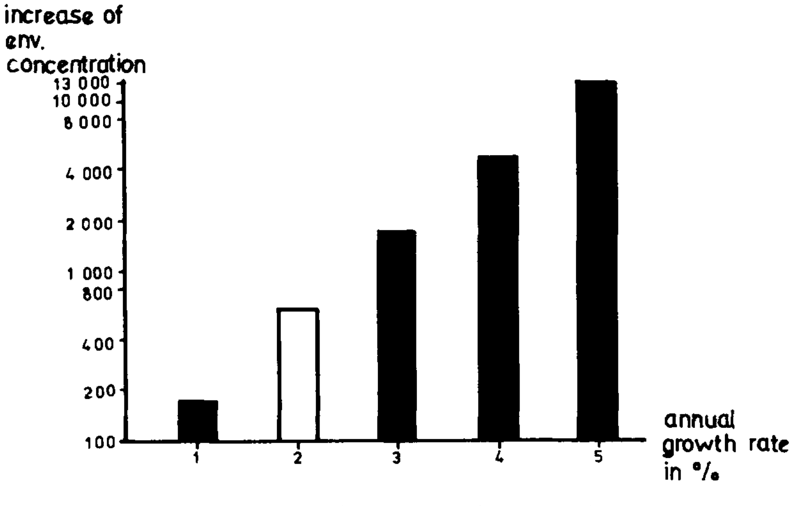

FIG. 2. Forecast of environmental concentrations.

TABLE 5

CHEMICAL AND ENVIRONMENTAL FACTORS INFLUENCING BIODEGRADATION

Chemical	Environmental
Chemical structure	Composition and status of biological system
Concentration of chemical	Natural population
	Selected microorganisms
Temperature	Concentration of microorganisms
Oxygen supply	Adaptation
pH Value	Carbon sources
Absorption to organic and inorganic particles	
Bioaccumulation	
For soils	
Class	
Redox potential	
Layer	

in the environment, although they are indicative for a low environmental persistence of benzene.

It is frequently claimed that microorganisms play the most important role by far with respect to degradation and mineralization of chemicals in the environment. This statement must be doubted for energy reasons—that is, the energy available in biological systems versus solar energy in the atmosphere and on land surfaces. Parallel to this argument goes the argument of routes of chemicals in the environment: soil or water as the primary medium where chemicals go upon release, or the atmosphere, where no significant microbial degradation capacity is expected. Since there are furthermore secondary transport phenomena from one medium to another, both the biotic and abiotic (sunlight) degradation need attention (Table 5).

For testing the degradability of chemicals in water a number of feasible tests are available that are internationally accepted. It is furthermore generally accepted that these biodegradability tests, modified OECD screening test, Afnor, MITI, Sturm, and closed-bottle tests, are predictive for the environment, at least for basic classification as readily, inherent, or nonbiodegradable.

Realizing the number of factors influencing the biodegradation of chemicals, any feasible, simple test procedure must have certain limits or drawbacks. Thus benzene cannot be tested in the OECD screening or the Afnor tests due to its volatility in the open systems. The closed-bottle test is analytically inaccurate, the Sturm test is analytically unrefined, and, as to the MITI test, there are some arguments concerning the microbial population.

Thus benzene seems to be not frequently tested for its biodegradability despite the vast number of metabolism and toxicokinetics studies. Benzene is not even included in the 1979 MITI list of tested chemicals for biodegradability and bioaccumulation. In this list, however, xylene and biphenyl are classified as "confirmed biodegradable," so that it can be expected that benzene will be too, using the MITI test.

We have developed a test system using ^{14}C-labeled chemicals, surveyed in Fig. 3, which comprises so far a total of six different tests aiming at the comparative

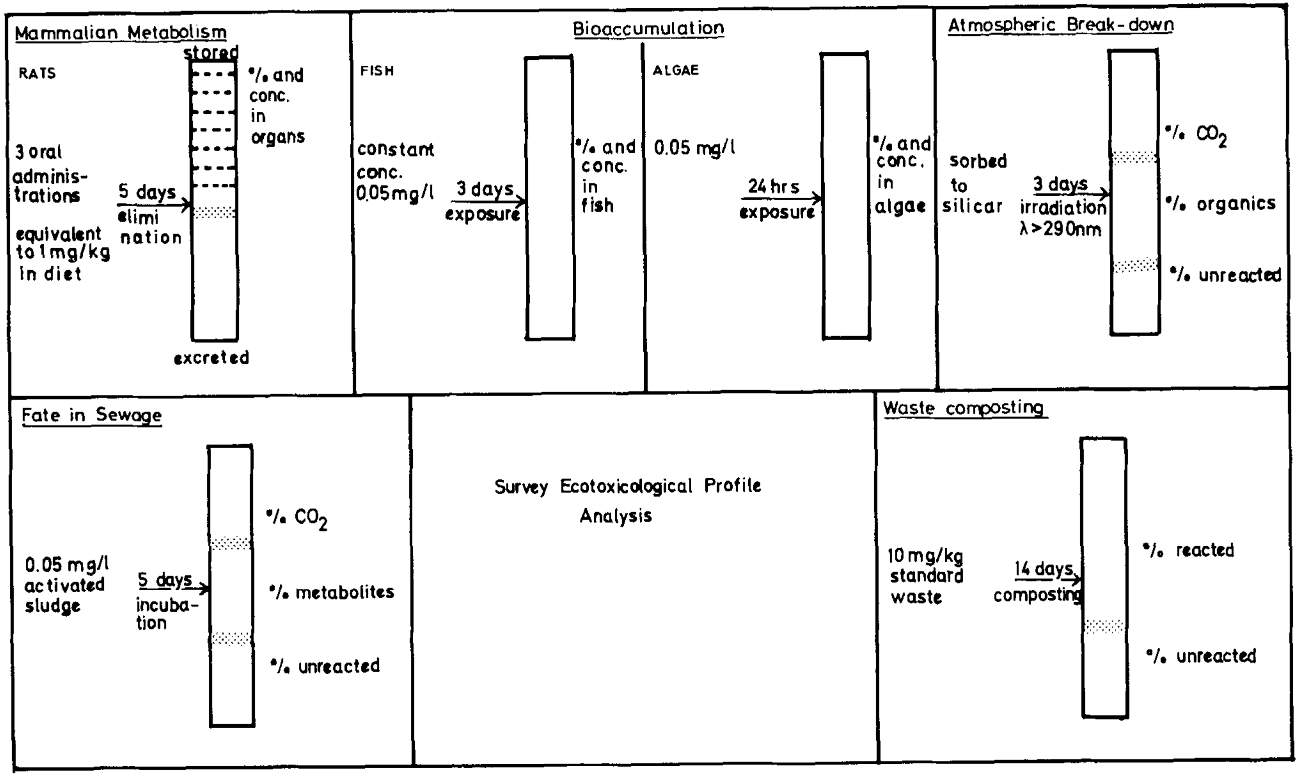

FIG. 3. Survey ecotoxicological profile analysis.

TABLE 6

ECOTOXICOLOGICAL PROFILE ANALYSIS: DEGRADATION OF AROMATIC COMPOUNDS

Chemical	Activated sludge ($\% \ CO_2$)
Benzene	29.0
Biphenyl	9.1
Aniline	37.0
Nitrobenzene	1.7
p-Nitrophenol	1.4
Hydroquinone	7.6
Hexachlorobenzene	3.0
Pentachloronitrobenzene	7.0
2,4,6,2',4'-Pentachlorobiphenyl	1.2
2,5,4'-Trichlorobiphenyl	0.5
2,2'-Dichlorobiphenyl	6.6
Pentachlorophenol	0.5
2,4,6-Trichlorophenol	0.1
p-chlorobenzoic acid	5.4
2,4-Dichlorobenzoic acid	0.3
2,4-Dichlorophenoxyacetic acid	0.1
p-tert-Butylphenol	4.9
2,6-Di-*tert*-Butylphenol	7.7
Di(2-ethylhexyl)phthalate	1.0

assessment of chemicals with respect to mobility, accumulation, and degradation (*8*). Benzene has been screened in this system of tests (*9*).

The biodegradability test of the ecotoxicological profile analysis is performed in a closed system, thus allowing the investigation of volatile compounds. Since the chemicals are principally used in ^{14}C-labeled form, there is no limitation with respect to solubility. The inoculum used is based on activated sludge from municipal sewage treatment. The test duration is only 5 days, whereas it is in the range of 20 days in the OECD-adopted tests.

The data given in Table 6 for the mineralization of aromatic compounds clearly demonstrate that benzene is readily biodegradable. The data have a high accuracy (safety margin) since only $^{14}CO_2$ is given. Any losses in the material balance are not included in the figures on degradation—they are, however, included in the tests using DOC (dissolved organic carbon) analysis. In the profile analysis test, benzene shows more than three times the biodegradability of biphenyl. Since biphenyl is confirmed biodegradable in the MITI test, there is, consequently, no question concerning the ready degradability of benzene.

Our degradability test, being performed in a closed system, does not provide data on volatilization from surface waters. Since ^{14}C-labeled chemicals are used, it gives, however, indications of the additional elimination of test chemicals from the aqueous phase into the sediment or sludge by analyzing water-insoluble radioactivity in the sludge. This is calculated as the ratio between residual radioactivity concentrations upon termination of the test in water and sludge. For the aromatic chemicals tested so far, the calculated figures range from 9 (2,4-dichlorobenzoic

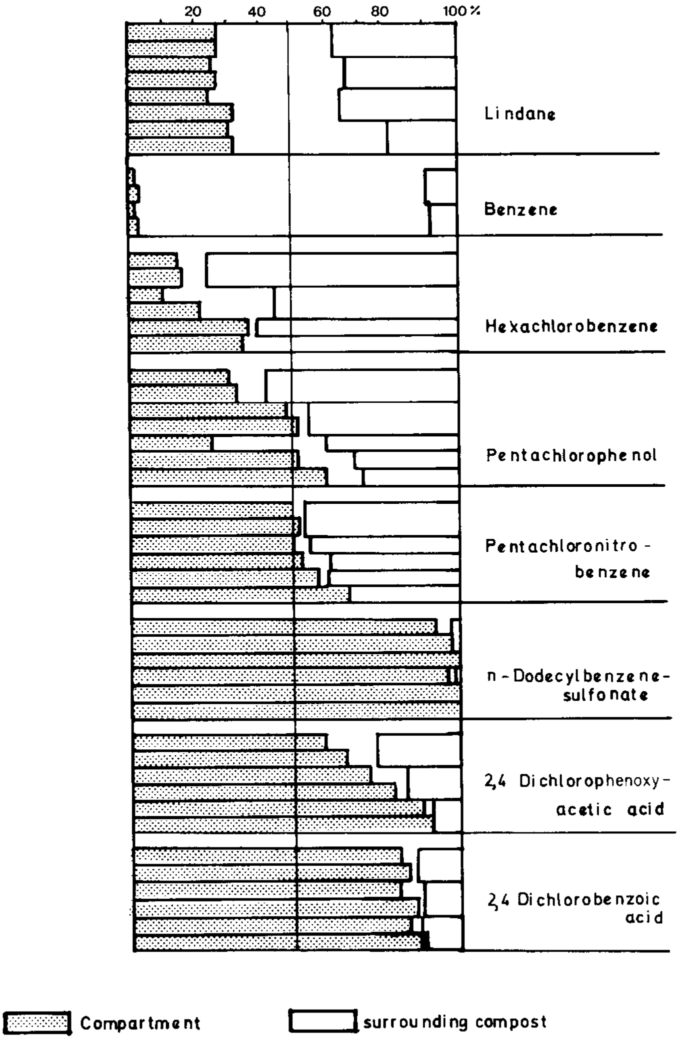

FIG. 4. Movement of chemicals upon waste composting.

acid) to 6700 (anthracene). For benzene it is 1500—thus showing a medium additional elimination from water by this route.

Concerning biodegradation in terrestrial systems (soil), there is so far no adopted screening test procedure. Due to the complex matrix, all tests in development or in validation will have to rely on the use of the test chemical in isotopically labeled form.

The waste-composting test of our profile analysis, originally designed to assess disappearance or persistence of chemicals upon waste composting, gives additional indications on metabolism and degradation by a variety of microorganisms and on the mobility of the chemicals in complex organic matrices.

Figure 4 shows for some chemicals the percentages remaining where they were before the composting process, that is, not moving at all; the percentages moving only short distances and then being adsorbed or retained; and, in between, the percentages volatilized. As compared to all other chemicals shown, benzene is highly mobile, and only very small amounts of it or its metabolites remain in the organic matrix (*10*).

Only 2 to 2.5% of the applied benzene does not move, 8 to 9% moves in the surrounding compost, and 35% is volatilized as benzene or organic derivatives. The missing 45–47% may be volatilized as $^{14}CO_2$, which cannot be easily identified in this test due to the great amounts of CO_2 formed from degradation of the organic matrix.

For the topic of this paper, this fact and the well-established volatility of benzene from waters clearly show that benzene, as well as its metabolites, does not remain in water or soil and that the fate in the atmosphere is of highest significance for the total balance of degradation in the environment. This is also confirmed by the results of other profile analytical tests (*9*):

—quantitatively negligible retention in rats, namely 1.5% 2 days after a 3 day dosing period,

—no accumulation or adsorption in algae,

—no accumulation of parent compound or metabolites in fish, with an accumulation factor in 3 days in the range 1 to 10.

Photochemical Degradation

Scientific background: Since several scientific concepts are in use to assess the photochemical or atmospheric fates of organics, and since this leads to certain discrepancies even in scientific discussions, I would like to give some background discussion to this important area.

Atmospheric chemistry. This made great progress during the last two decades. Many research groups have investigated the reaction mechanisms, reaction chains for formation and disappearance of active species, and radicals under sophisticated high-vacuum laboratory conditions. Mostly inorganic gases and simple organic molecules, alkenes, arenes, and a few saturated hydrocarbons, have been intensively studied. As a result of these enormous efforts, which were supported by environmental monitoring for the investigated "air pollutants," we have now a well-advanced understanding of the formation and degradation of photochemical smog and we have appreciable basic scientific knowledge on the reactivity of some chemicals in the atmosphere and also possible reactions of chemicals (*11*). For instance, half-lives have been confirmed by field measurements. However, physical and chemical processes in the atmosphere are of such complexity that even results of thoroughly performed field tests with simple chemicals like SO_2 are not absolutely doubtless. Thus it is evident why the chlorofluorocarbon–ozone hypothesis is so difficult to evaluate. There are contradictory scientific results: the chlorine radical reaction chain consuming large amounts of ozone in the stratosphere (*12*) and, on the other hand, the fast mineralization of these chemicals even without sunlight on natural surfaces in the troposphere, where no problems arise from this destruction (*13*).

Range of chemicals. In atmospheric chemistry for a long time only gases or chemicals with a high vapor pressure were considered. This is appropriate given the total mass of chemicals in the atmosphere—the large amounts of inorganics, natural hydrocarbons, hydrocarbons having both natural and industrial origin (carbon tetrachloride), and industrial base chemicals.

However, concerning the number of chemical individuals, this limitation to high-vapor-pressure chemicals is inappropriate. Also chemicals with low vapor pressure, even below 10^{-6} bar, like DDT, HCB, PCBs, and showing some persistence against biodegradation, enter the atmosphere in significant amounts. These constitute by far the larger number of produced chemicals (90%). About one-half of these chemicals can be evaporated into the air within one season after application to soil (*14*).

State of chemicals in the atmosphere. In the concepts of atmospheric chemistry it was assumed that only gas reactions play a role in the atmosphere. Consequently, wall reactions in experiments were claimed to result in artificial, noninterpretable results. Since an unequivocal sampling of air for particle-bound and gaseous chemicals separately is very difficult, there are in fact only estimates concerning the state of chemicals as monomolecular gases, clustered gases, and particle-bound gases. It has been estimated that the air column over 1 m^2 of land surface has an active surface of particles of another 1 m^2, and that these surfaces together might adsorb 10% of the present organics. This, however, needs differentiation from chemical to chemical and more thorough investigation.

Methods of Investigation

It is generally accepted among experts that there is no ideal method available for investigating the fate or atmospheric half-lives of chemicals. The most sophisticated methodology used, apart from field trials, is so-called smog chambers, where the reactive species and the first degradation step of a high-vapor-pressure chemical are carefully followed. One experiment can run, however, only for a few hours to keep the data conclusive. Since all physical and chemical factors are controlled the resulting data are scientifically sound, but it must be stated that even the most sophisticated smog chambers do not really simulate the entire atmosphere.

From the whole set of available data it was concluded that the reaction with OH radicals plays the most important role in the first atmospheric attack on chemicals. Primary photochemical reactions or reactions with other active species are estimated to be of minor significance (*11*).

The reason for the OH radical concept is, on the one hand, the high concentration of 10^5–10^7 OH radicals per cubic centimeter and high reaction constants found for those chemicals which have short half-lives in smog. There are further arguments to follow this concept, though one argument against it should be mentioned: it is not necessarily true that the first attack to alter a chemical has the lowest rate constant. There may be more persistent intermediates so that a chemical might be ranked incorrectly.

The OH rate constants have been measured for a larger number of chemicals with sufficient vapor pressure. Taking uncertainties into account, these chemicals were classified into five groups from short to long half-lives (*11*). In this classification benzene is in the third group, where the atmospheric half-life range is 0.1 to 1 day.

Table 7 gives a very short summary of the atmospheric chemistry investigations with benzene, showing an atmospheric half-life of less than 1 day.

Contrary to this sophisticated methodology, many feasible experimental condi-

TABLE 7

BENZENE HALF-LIVES: SMOG CHAMBER AND REACTIVITY WITH ACTIVE SPECIES

$OH^{\cdot}$ reactivity	$t_{1/2}$ (days)
k_{OH} (mol^{-1} sec^{-1}) = 0.85×10^{-9}	
Half-life according reactivity scale (Pitts)	0.1-1
Half-life calculated	0.67
Half-life calculated O_3 reactivity	50,000
Half-life calculated $O(^3P)$ reactivity	1,400
$k_{smog\ chamber}$ (mol^{-1} sec^{-1}) $\leq 2.3 \times 10^{-9}$	
Half-life	<1

tions have been used to study primary or secondary photochemical reactions of organic chemicals.

In the pesticide area, e.g., there are many examples of reactions in the laboratory that have an environmental significance. For instance, dieldrin isomerizes in sunlight on leaves, etc., to photodieldrin in the same way as in a test tube when irradiated with sunlight or artificial light. Organovinylphosphates isomerize in nature from *cis* to *trans* isomers in sunlight as they do under laboratory conditions in solution, with the effect that they lose their insecticidal activities; some change thus to effective herbicides. This reaction can be quenched in nature and in the laboratory. On the basis of this proven environmental significance, laboratory methods have been designed to measure the disappearance rate of organics in presence of sunlight or artificial light. This has been done for more than 10 years in many countries by many research groups under a large variety of experimental conditions, which are sometimes similar to the methods of preparative photochemistry.

Some groups have also studied the photochemical disappearance of chemicals in "gaseous phase" in small-volume flasks. According to the physicochemical understanding, these experiments result in too high degradation rates due to wall reactions.

We have used a gas volume of 20 liters to study the photochemical degradation in "gaseous phase" (*15*). With dry clean air or oxygen and a concentration of 100 ppm benzene we could not find any disappearance of benzene within 6 days irradiation with wavelengths corresponding to tropospheric sunlight ($\lambda > 290$ nm). This is an argument against the wall reaction concept. When using higher energies (quartz filter) and irradiating with wavelengths above 230 nm, the half-life of benzene was 6.5 hr. Using again ***tropospheric wavelengths*** and adding chemicals that produce active species, benzene half-lives were between 4 and 5 hr. Nojima *et al.* (*21*) used a 1-liter flask, wavelength > 300 nm, 1000 ppm benzene, and 200 ppm NO and found a degradation of 30% within 5 hr. Realizing different concentrations and irradiation intensities, the data are in good agreement, but the half-lives are short when compared to the 0.69 days calculated from OH reactivity. It should be emphasized, however, that no laboratory method, regardless of its complexity, gives absolute data, but that half-lives have to be calculated using correction

TABLE 8

PHOTOCHEMICAL HALF-LIVES OF BENZENE

Irradiation conditions		$t_{1/2}$ (hr)
Gaseous phase		
100 ppm benzene	$\lambda > 230$ nm	6.5
+10–110 ppm NO_x	$\lambda > 290$ nm	5
+10–100 ppm SO_2	$\lambda > 290$ nm	6
+10–100 ppm NO_x + 5 ppm isobutane	$\lambda > 290$ nm	4
Moving bed rector		
dry silica gel	$\lambda > 290$ nm	16

factors measured with reference compounds. For degradation rates in smog chambers, toluene or *cis*-2-butene are frequently used.

The last line in Table 8 shows the half-life experimentally measured for benzene in a moving bed reactor of 6-liter volume. In this experiment there was intentionally a great active surface of 200 g carefully dried silica gel, on which 0.78 ppm [^{14}C]benzene was absorbed. The measured disappearance of benzene upon irradiating with tropospheric wavelengths showed a half-life of 16 hr, *quite exactly the half-life calculated from the OH rate constant* (*16*).

Photomineralization

Realizing the capacity of the energy of sunlight to degrade chemicals and the need to have knowledge on the total degradation and mineralization of organic chemicals, we have developed several complementary methods. One point that needs emphasis shows the need for such methods. The production figures of DDT during the last decades are well known, including the distribution of their metabolites on the earth, which represents not more than some of the total volume. It was a big discussion where all the rest was left. After having found that DDT and its metabolities are completely destroyed in the presence of light and decompose to CO_2, the photomineralization rate and practical environmental conditions can be correlated with the degree of decomposition to CO_2 under standardized laboratory conditions. This gives indications for the environmental significance and can of course be extended to any other chemical in question. This shows that there are ways to establish the environmental relevance of photochemical degradation reactions in the laboratory as for any other laboratory test procedure.

The methods of atmospheric chemistry are much too complicated to investigate the degradative pathways to final CO_2. Reactions in organic solvents lead to artifacts and are not predictive to the environment, and irradiations with environmental wavelengths in aqueous solutions do not easily result in the terminal CO_2. Therefore we followed the concept of using the absorbed chemical and measured the rate of CO_2 formation. Under standardized conditions this gives relative data of ranking for photomineralization. Compared to reference compounds it gives indications on the environmental stability of a used chemical, including all degradation intermediates.

Concerning the relevance of the photomineralization test methodology, it was shown that with dry silica gel benzene half-life was identical to the OH reaction constant-based half-life. Since no other methods or data are available to measure the CO_2 conformation rate from organics in the atmosphere, there are no other reliable data for comparison. Thus, despite the entirely different concepts and data, ranking according to OH reaction constants was compared to the ranking in the ecotoxicological profile analytical photomineralization test.

Table 9 shows a set of original photomineralization data obtained in the profile analysis test using 50 ppb ^{14}C chemical on silica gel and 17 hr irradiation (*8*, *9*). Chemicals, including methanol, acetic acid, chlorinated benzenes, aniline and others, where OH reactivity, smog chamber, and photomineralization data were available, were compared with the respect to the ranking, using benzene as reference. Ranking was identical for most; in three (F, Cl-hydrocarbons, carbon tetrachloride) photomineralization was higher, and for one (aniline) it was lower (*17*). It must be emphasized, however, that in the photomineralization procedures the integral degradation pathway is assessed and not only the initial step. Consequently the CO_2 formation rates are much lower than the half-lives of parent compounds. There may be examples where the reaction steps leading to CO_2 are faster and others where they are slower than the initial reaction. *Thus the photomineralization has a high relevance if the degradation intermediates are to be included in the evaluation of atmospheric degradability.*

Figure 5 shows the kinetics of benzene disappearance and the formation of intermediates and CO_2. The reaction conditions were those leading to a benzene half-life of 16 hr (*16*). The curves show that there is an initial buildup of a high amount (45%) of intermediates with significantly delayed CO_2 formation. Consequently the

TABLE 9

ECOTOXICOLOGICAL PROFILE ANALYSIS: DEGRADATION OF AROMATIC COMPOUNDS

Chemical	Photomineralization (% CO_2)
Benzene	5.0
Biphenyl	9.5
Aniline	46.5
Nitrobenzene	6.7
p-Nitrophenol	39.1
Hydroquinone	57.4
Hexachlorobenzene	1.5
Pentachloronitrobenzene	43.0
2,4,6,2′,4′-Pentachlorobiphenyl	5.2
2,5,4′-Trichlorobiphenyl	5.9
2,2′-Dichlorobiphenyl	3.5
Pentachlorophenol	62.0
2,4,6-Trichlorophenol	65.8
p-Chlorobenzoic acid	6.3
2,4-Dichlorobenzoic acid	—
2,4-Dichlorophenoxyacetic acid	26.2
p-*tert*-Butylphenol	46.8
2,6-Di-*tert*-Butylphenol	29.5
Di(2-ethylhexyl)phthalate	1.6

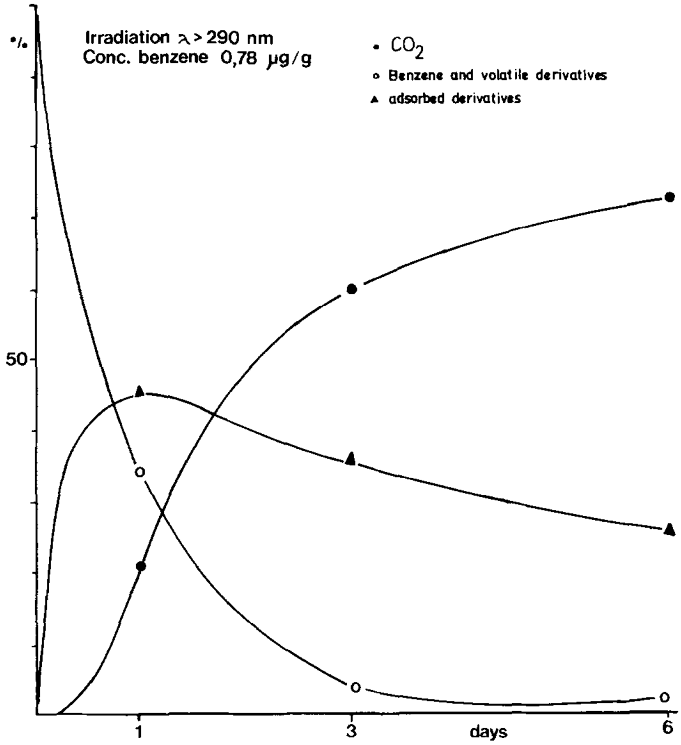

FIG. 5. Photomineralization of benzene on silica gel. Irradiation, λ > 290 nm. Benzene concentration, 0.78 ppm. ●, CO_2; ○, benzene and volatile derivatives; ▲, adsorbed derivatives.

time for 50% CO_2 formation is 48 hr. According to our understanding of the assessment of chemicals, the CO_2 formation rate should be measured for all chemicals rather than the initial degradation step.

TABLE 10

CORRELATION BETWEEN PHOTOMINERALIZATION OF BENZENE, WATER CONTENT OF ABSORBENT SILICA GEL, AND OTHER CARRIERS

Carrier	Photomineralization (% CO_2)
Six-day irradiation, λ > 290 nm	
Silica gel	
Dried 370°C	72.7
Dried 150°C	45.7
Commercial (3.2% water)	55.8
Commercial + 10% water	11.8
Commercial + 50% water	12.0
Thirty-day irradiation, sunlight	
Natural sand A (0.2% water)	<1
Natural sand B (0.3% water)	<1
Silica gel (3.2% water)	9.7

TABLE 11

COMPARISON OF METHODS FOR TESTING PHOTODEGRADABILITY

Test method	Phase	Effect under investigation	Precondition to the test compound	Critical points	Reference compound
Fujiki	Gas	Disappearance of the parent compound	Sufficient vapor (1 Torr corresponds to 0.06 mmol/liter, e.g., 6 mg/liter with mol. wt. 100)	Quality and intensity of artificial light	—
GSF	Adsorbed phase	Formation of the final breakdown product CO_2	Low vapor pressure in presence of silica gel at a concentration of 4 μmole/g; otherwise modifications (correction, *or* other purging/irradiation time program)	Quality and intensity of artificial light	Pentachlorophenol
EPA	Aqueous solution	Disappearance of the parent compound	Sufficient water solubility for homogeneous aqueous solution	Dependence of weather conditions	

Table 10 gives some data for varying experimental conditions. Quantitative assessment of these is not possible, and qualitatively it is shown that benzene is even mineralized under the least favorable conditions.

Finally, we would like to present the data resulting from the simple and feasible photodegradability test methods as adopted by OECD. Table 11 gives a short description of the three methods: The Fujiki (*18*) and EPA (*19*) methods to test for the disappearance of the parent compound, and the GSF test for mineralization as discussed. The GSF test is applicable for all organics, needs careful performance, and needs some corrections only for gases, whereas in the Fujiki test a sufficient vapor pressure is necessary, and in the EPA test a sufficient water solubility of the test chemicals is needed.

TABLE 12

BEHAVIOR OF BENZENE IN PHOTODEGRADATION TESTS

Test and conditions		Degradation
GSF tests on silica gel $\lambda > 290$ nm	Screening 5 mg/12 g SiO_2 3 hr irradiation	0.4% CO_2
	Profile analysis 50 ppb 17 hr irradiation	15% CO_2
	Moving bed reactor 0.78 ppm 6 days irradiation	55.8% CO_2
Fujiki test 10 ppm benzene in air	19 hr $\lambda > 290$ nm	n.d.
	24 hr $\lambda > 275$ nm	n.d.
	150 hr $\lambda > 275$ nm	50%
	24 hr $\lambda > 230$ nm	38%

The data shown in Table 12 for the GSF and Fujiki (*20*) tests (EPA test not performed) demonstrate that these test procedures do not result in a too-high degradability. Upon testing a larger number of chemicals it is shown that they allow a certain ranking for degradability with the differences in interpretation of data as discussed above, and that the tests are complementary.

As a conclusion of the different data presented on mobility of benzene and its degradation, it can be stated that:

—benzene is readily biodegradable,
—its fate in the atmosphere is of major importance,
—the atmospheric half-life of benzene is less than 1 day,
—the time for 50% mineralization in the atmosphere is likely to be about 2 days.

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