Some of these aerosol reaction channels lead to detoxification of the nerve agent; others would not. Kinetic and product information are almost entirely lacking. Since maximum rates for contacting the aerosol exceed those of net gas-phase oxidations, the heterogeneous reactions are of potential import. We classify them as a high research priority. The collective aerosol interaction possibilities are referred to along with gas-phase oxidations in Figure 10.

The fractional volume occupied by particles in an urban atmospheres is vanishingly small. An RSP mass of 100 $\mu g\ m^{-3}$ translates to a water equivalent of volume of $10^{-10}\ cm^3$ (aerosol) cm^{-3} (air). The Henry's Law constants for organophosphorus pesticides and nerve agents are sufficiently near unity that partitioning into the aerosols is not favored. Reactions must proceed rapidly for mass transfer from the vapor phase to be significant. A small solubilized portion of highly toxic substance may nevertheless be of interest. Given the enormous uncertainties in sarin heterogeneous chemistry, entry into the aqueous phase could actually have a stabilizing effect relative to the vapor. Agent contained in particles is isolated from gaseous oxidants. Brownian approach to ground and structural surfaces is slow so that deposition velocities are reduced. If the molecule does not decompose in or on the aerosol, its lifetime may rise to on the order of weeks against deposition (Seinfeld, 1986). Most large metropolises including Los Angeles and Mexico City ventilate in one to two days. Long-range transport of sarin may be achievable toward suburban and nonurban areas.

Discussion

Through analyses of (1) the atmospheric chemistry of organophosphorus pesticides, (2) structure-reactivity relationships for atmospheric hydrocarbons, and (3) aerosol heterogeneous physicochemistry, we have established likely pathways for the degradation of sarin in urban atmospheres. Some limits have also been placed on their rates. Time constants could be as short as one hour for hydrogen abstraction by the hydroxyl radical and minutes for rapid reaction at particle surfaces.

We have stressed that our estimates for sarin loss time scales are quite uncertain. They of course depend initially on highly variable local concentrations of several types of reactant. More important, physical parameters defined in the loss mechanisms are poorly constrained. Rate constants for hydrogen atom abstraction by hydroxyl cannot be accurately computed because the electron withdrawing capacity of the phosphorus fluoridate group is unknown. Neither the efficiency for sticking at aerosol surfaces nor the rate of removal within particles has been measured. Laboratory experiments and improved theoretical treatments could reduce the error bars inherent in our work.

Rates for the hydrogen abstraction have been based largely on a handful of electron induction correlations (e.g., Atkinson, 1987). While our approach is comparable to the state of the art in atmospheric chemistry, more complete evaluation of the sarin structure could illuminate the role of the phosphate group in determining the electronic distribution on organic side chains. We would envision employing the sophisticated molecular modeling software now on the market. Program names include MOPAK and ALCHEMY. Reactions at the phosphorus center have not been investigated here. The inorganic chemistry database could reveal analog molecules for which gas phase reaction rate constants are known (e.g., Cotton and Wilkinson, 1972). The lack of interactions between atmospheric oxidants and the P atom in the pesticide species is an indication that decomposition of the methyl and isopropyl groups dominate. However, closure demands some examination of the inorganic literature. It should be noted that we have avoided mention of the temperature dependence of the gas-phase rate constants drawn upon or estimated. The assumption of constant temperature can be rationalized to some extent by the complexity of the general problem. Ultimately, however, temperature effects must be incorporated into models of sarin chemistry/transport. This means that activation energies must be deduced in addition to absolute rates.

Laboratory studies can readily be conceived which would yield values for the critical rate processes. They would be patterned after the techniques of basic atmospheric chemistry research (Finlayson Pitts and Pitts, 1986 and 1997; Ravishankara, 1997). Studies of gas phase kinetics for sarin could provide data on rate constants for hydroxyl attack and on product distributions. They would be cumbersome and expensive relative to their predecessors; exposure of the experimenter to the reactant would have to be prevented. However, it is said that the sarin used in the Tokyo incident was synthesized in a standard fume hood (TSSI, 1997). Furthermore, the syntheses involved in preparation of atmospheric chemistry experiments are often dangerous and toxic vapors are familiar. Classic heterogeneous chemistry experiments are in order. Flow tube and Knudsen cell reactors are typical equipment. The complexity of the experiments might be reduced through the analog strategy employed to investigate OP pesticide kinetics. Sarin simulants have been developed with varying degrees of realism and toxicity (Das Grupta et al., 1988). Experiments conducted on reactive surfaces could also contribute to understanding of deposition processes for the nerve agents.

Embedded in the issue of product distributions is yet another level of uncertainty – that of the product toxicities. We have essentially restricted ourselves to the comment that cholinergic activity requires a viable leaving group (Fest and Schmidt, 1973; Metcalf, 1982). Since the products themselves are almost entirely mysterious; their potential as esterase inhibitors has not been quantified. Toxicity can of course be measured clinically (Cherniak, 1988). The experiments might be coupled to controlled laboratory sarin oxidations. Molecular modeling can also clarify cholinergic potential.

It will be remembered by the reader that we have consciously based our development solely on the open scientific literature. Indications are that the urban chemistry of nerve agents has not been investigated in detail (Lohs, 1980; Ministry for Foreign Affairs of Finland, 1985). However, we recognize that some of the studies we advocate may have been performed within the defense establishment. Our open research on sarin is justified by the immediate threat of terrorist releases, combined with the inaccessibility of any relevant classified information.

Our ultimate goal is to simulate the interactions of sarin with a city atmosphere in a three-dimensional tracer transport context. The terrorist potential of the chemical and biological warfare agents (TSSI, 1997) has lately inspired the development of ultra-high resolution models of flow in the urban regime (Daisey et al., 1997). Several of us are involved in representing the atmospheric motions along buildings and streets near major targets. Resolution is approaching ten meters in our programs. A tool relied upon in such detailed flow simulations is the HIGRAD advection routine, a descendent of early positive definite transport algorithms employing reverse advection velocities to counter numerical diffusion/dispersion (Smolarkiewicz, 1983; Smolarkiewicz and Rasch, 1991). Other groups have ten meter capability as well (Hoydysh and Dabbert, 1994; Theurer et al., 1996; Daisey et al., 1997). As our sarin breakdown schemes evolve, they can be inserted as multiple tracers into the transport codes. A potential complication is that higher concentrations of the agent near-source will impact oxidant chemistry locally. The phenomenon may be discernible on the fine scale. Initial hydrogen abstraction steps are net losses of radicals in the HOx family. During decomposition of the sarin structure, hydrogen atoms are released as oxides so that back-filling takes place (Crutzen, 1988; Elliott et al., 1994 and 1996). It may be necessary to couple sarin and its byproducts into a full urban photochemistry mechanism. In other words, it may not be feasible to handle oxidants off-line. We plan to begin adding the nerve agent and its decay products to atmospheric chemistry schemes in low-dimensionality test runs.

The incorporation of agent chemistry into a three-dimensional street canyon scale model will constitute a valuable endeavor in and of itself; the potential for terrorism is quite real. However, we anticipate benefits to urban air quality models as well. Air pollution problems have most often been simulated over entire cities and at kilometer resolution or coarser (e.g. McRae et al., 1982). Localized pollution problems can be subgrid in scale, and nonlinearities associated with near-source levels of specific compounds are smeared through averaging. Our programs should be adaptable to the study of air quality at the street corner level.

Summary

Terrorism employing chemical and biological weapons is fast becoming a reality in major metropolitan areas around the world (Department of Commerce, 1994; Ember, 1995; TSSI, 1997). Attacks typically involve dissemination of an agent though the urban atmosphere so that photochemical and phase transformation are possibilities in some cases. Products of the changes may still be toxic and persistent. As an example of the complexity which will be attained during agent oxidations and of the degree to which details can be understood from first principles, we have performed an investigation of atmospheric chemistry for the nerve gas sarin. The molecule has seen documented military applications in recent years (Ember, 1993; McCarthy, 1997). It has been deployed in a major urban zone in peacetime, and that has caused massive casualties (Okumura et al., 1996; Yokoyama et al., 1996). The chemical structure of sarin happens to be reasonably simple (Verweij et al., 1979) and is similar to a class of pesticides for which rates of atmospheric transformations have been measured (Winer and Atkinson, 1990). We set as objectives the definition of pathways for sarin decay in urban air and the estimation of uncertainties in their rates. Initial emphasis is placed on information available in the open literature, since time may be of the essence in analyzing terrorist situations. Followups are planned in the context of defense sources.

Our work begins with a review of the development and uses of nerve agents over the decades (Hoeber and Douglass, 1978; Dunn and Sidell, 1989). As background, the mechanism of cholinesterase inhibitions is sketched for the nervous systems of higher animals (Metcalf, 1982). The recent urban sarin incident in Tokyo is then described in full

(Ember, 1995). It is noted that the Tokyo release mechanism was exceedingly rudimentary. Liquid agent was left to evaporate from open paper bags (TSSI, 1997). Most of the several thousand injuries were caused by sarin dispersed through the vapor perase (Ohbu et al., 1997). A study scenario is designed based on the Japanese incident which allows for chemical and phase changes to take place. It consists of outdoor injection into a city atmosphere in the morning, during the period of decreasing stability of the nocturnal boundary layer and increasing photolytic activity. Sarin is assumed to begin its transport as a gas, to react with major oxidant species, and to interact with pollutant particles. With a generic case at hand for study, we move on to the identification of channels and calculation of rates.

As a first step in elucidating the sarin atmospheric chemistry, we outline current knowledge of the transformations of the analog organophosphorus pesticides (Lewis and Lee, 1976). They have been closely scrutinized as hazardous pollutants subject to long-range transport, particularly in California's Central Valley and Sierra Nevada mountains (Glotfelty et al., 1990; Aston and Seiber, 1996). The OP insect control species differ from the nerve agents in that they are released into the atmosphere in the thion ester form (Glotfelty et al., 1987). The more toxic oxon is meant to arise only in the guts of the target organisms (Metcalf, 1982). However, oxidation of the thion can occur incidentally in transit. It is the family of oxon phosphorus esters which is most dangerous (Seiber et al., 1989). Their atmospheric degradation has been quantified empirically and it occurs in on the order of hours to days depending on local conditions and on molecular structure (Woodrow et al., 1983). Overall breakdown mechanisms are not known, but initiation has been studied for model compounds such as trimethyl phosphate (Winer and Atkinson, 1990). Rate constants for hydrogen abstraction by the hydroxyl radical are consistent with the field studies. Direct photolysis and reaction with ozone appear to be slow. A footnote of some interest is that many known pesticide decay sequences lead to intermediates with toxicities equal to or greater than those of parent species (Seiber and Woodrow, 1994).

At this point in our investigation we pinpointed the major reactants accessible to organic vapors in the urban environment (Finlayson Pitts and Pitts, 1997). The pesticide research suggests that hydroxyl, ozone, and ultraviolet/visible photons should all be assessed. To this list we add the variety of urban aerosols. Concentration ranges are set for the city reactants through a sampling of results which have been obtained in two of the world's most populous and polluted areas, the Los Angeles basin and Valley of Mexico. We selected these as baseline locations because they are representative of domestic and developing megacities, respectively, and because we have participated in the evaluation of their vexing but distinct pollution problems (MARI, 1994; Elliott et al., 1997a and 1997b). Nonlinearities in the organic/oxidant/ozone system are outlined (Blake and Rowland, 1995). The aerosol is treated as a set of ammonium nitrate and sulfate equilibria (Russell et al., 1983) with low volatility organics superimposed (Pandis et al., 1993). The culmination is a table of upper and lower concentration limits for the specified reactants at midday.

The heart of our sarin work consists of structure-reactivity estimates for the rate of hydroxyl radical attack upon attached hydrogen atoms. We argue that the ozone and photolysis reactions will be less important. The trimethyl phosphate rate constants (Winer and Atkinson, 1990) are cast into activation enthalphy correlations with more familiar atmospheric organics such as alkanes and hydrocarbon oxygenates (Atkinson, 1987; Gaffney et al., 1986). Classical free energy relationships are called upon for guidance, including the Hammett theory for benzoic acid derivatives and inductive effects in halogenated straight chain alkanoic acids (Fieser and Fieser 1961). The phosphorus ester linkage seems to behave through induction as a mild electron donor relative to the proton. It resembles carbon esters and alcohol substituents in this regard. One thus expects abstraction of at least some hydrogens from the sarin alkyl group at 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Winer and Atkinson, 1990). On the other hand, strong electron withdrawal by the fluoridate will countermand the activation. The degree of the counter-effect is difficult to quantify. We therefore set the abstraction rate constant at 10^{-12} to 10^{-11} as a fast limit for an initial oxidation step. The sarin lifetime varies from as little as hours upward to many days given the uncertainties and the range of hydroxyl concentrations set for the urban atmosphere. The molecule is photochemically stable under the morning inversion in our standard scenario and begins to degrade as solar angles change.

Products resulting from hydrogen abstraction cannot be predicted. The proton interior to the isopropyl grouping is likely to be removed first because its neighboring methyl groups serve as electron donors. The radical which remains could fall apart through well-known atmospheric oxidation steps to a small oxygenate such as acetone and a sarin hydrolysis derivative. The acids that are produced through nerve agent hydrolysis are not toxic (Verweij et al., 1979). However, methyl hydrogens are numerous on the sarin skeleton and their loss could be important channels for statistical reasons (Gaffney et al., 1986). Oxidation of the methyls would lead by analogy with simple alkanes to aldehyde or nitrate moieties. Their structures are sufficiently similar to that of sarin to retain high toxicity. The critical factor is preservation of the fluorine-leaving group which permits esterification of the choline enzyme. Some perspective on the toxicity issue is provided by the medical and pesticide literatures, which consider biological effects as functions of small structural disparities (O'Brien, 1960; Vojvodic, 1973; Boskovic and Kusic, 1980; SIPRI, 1980).

Other gas-phase oxidation pathways and product lines can only be speculated upon. The hydroxyl radical could conceivably attack the phosphorus atom. A methyl radical might be displaced. The phosphorus-to-fluorine bond is a weak one subject to breakage (Cotton and Wilkinson, 1972). An addition to examining vapor-phase oxidation, we have computed rates for sarin transfer to the surface of the aerosol. The time scales are potentially faster than the hydrogen abstraction range. Urban particles are strong aqueous ionic solutions at relative humidity above about 50%. Hydrolyses and nucleophilic substitutions may deactivate sarin in the liquid phase (Verweij et al., 1979). Oxidation and photolysis reactions are possibilities as well (Brown, 1993), with unknown product distributions. Organic coatings (Pandis et al., 1993) complicate but may possibly expedite the entry of the nerve agent into aqueous particulates. Rates for aerosol uptake have not been measured. The fine mode of the urban size spectrum sediments only slowly and so could serve as a vehicle for long-range transport. We excluded fog interactions and wet deposition in rain from the present analysis.

A closing discussion distills some of the uncertainties in our manipulations and indicates avenues for further investigation. We have based our current characterization of vapor phase sarin loss pathways on a few energy correlations from rather early atmospheric research (Gaffney et al., 1986; Winer and Atkinson, 1990). Error bars might be narrowed through the application of more sophisticated energetic analyses. For example, desktop molecular modeling software now gives the individual chemist the ability to visualize electron densities for arbitrary compounds. Density maps could shed light on induction along the sarin backbone. It might also prove profitable to search inorganic as opposed to atmospheric chemical databases for rate information. Other means for reducing uncertainties are itemized as well. We performed our calculations solely for room-temperature energetics. Activation and enthalpy effects must be factored in. Laboratory experiments can be envisioned for the determination of nerve agent reaction rates and product distributions. They would resemble traditional work in atmospheric kinetics (Finlayson Pitts and Pitts, 1997) but would be more dangerous and expensive (Zapf, 1993). Product toxicities may be determined clinically (Tripathi et al., 1989), or through further molecular modeling, of the outstanding cholinergic microsymptoms (Politzer and Jayasuriya, 1986). Although particle contact rates are easily computed, rapid reactions in the aerosol are required to support mass transfer. Data on surface interactions are wholly lacking. Boundary processes such as adsorption and deposition have been largely ignored here as a means of achieving tractability. In the urban environment, surfaces and surface chemistry will be varied and must be accounted for (Crump and Seinfeld, 1981; Baldocchi et al., 1987; Taylor and Spencer, 1990; Taylor and Constable, 1994). Finally, we reiterate that we have not yet begun to exploit research by the defense establishment.

The discussion section also touches upon some ramifications of our findings. With hoaxes and real chemical/biological terrorist attacks now coming at regular intervals in world cities (TSSI, 1997), the atmospheric sciences community is mobilizing to produce incident models. Both indoor and outdoor computational fluid dynamics coding will be adopted (Daisey et al., 1997). Some groups are capable of simulating transport in the complex urban arena of building surfaces and street canyons to ten meter resolution or finer (Theurer et al., 1996; Daisey et al., 1997). Accurate portrayal of the dispersion of the nerve agents and their decomposition products will require complete decay schemes and a knowledge of the embedded uncertainties. It is even possible that the chemistry of sarin degradation will have to be coupled to that of city air, since high local organic concentrations could alter oxidant fields and so lead to nonlinearities. Our estimates here assume that sarin oxidation proceeds independently. Insights from such detailed studies of chemistry transpiring in urban air may ultimately hold benefits for general pollution research. Early steps for the incorporation of full agent physicochemistry into microscale models may include low-dimensionality demonstrations.

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Table 1. Some urban chem/bio agent release episodes in major cities.

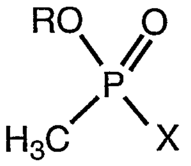
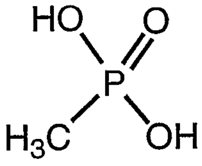
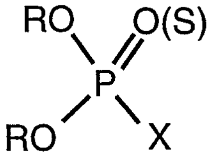
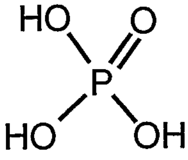
City	Agent	Type	Damages	Footnotes
Washington, D.C.	anthrax	biological	hoax	1
Tokyo, Japan	sarin	nerve	10 deaths	2
Tokyo, Japan	anthrax	biological	test	3

1. This hoax was carried out at the offices of the B'nai B'rith. A small container with the incorrectly spelled label "Anthracks" and a small quantity of an involatile liquid caused a large-scale building evacuation and required that emergency decontamination procedures be applied to many of the occupants.

2. The Tokyo sarin release occurred in subway cars and led to 5000 civilian casualties and the deaths of several first-responding employees. Details are given in the text.

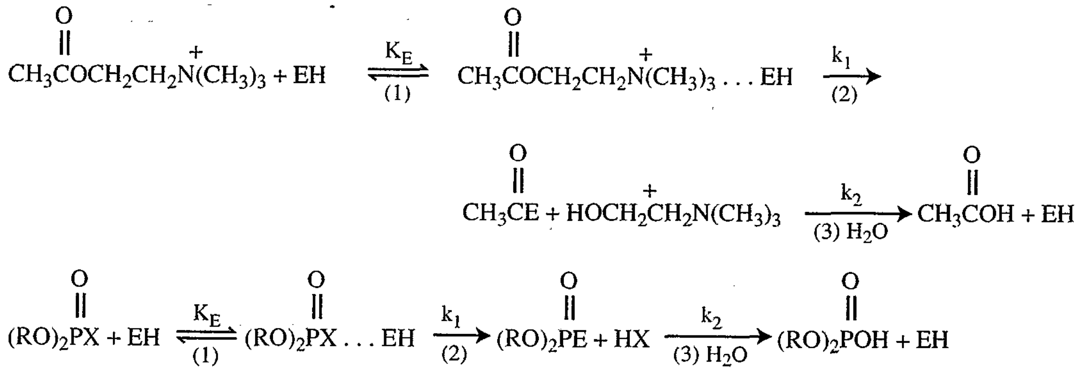
3. The rogue cult responsible for the subway sarin incident had been working to develop capabilities to deploy other weapons or nuclear devices and actually tested the release of the biological agent anthrax.

Table 2. General structures of nerve agents and similar pesticides with the related phosphorus acids (Verweij et al., 1979).

	Compound	**P Acid**	
Nerve Agents			**(Methylphosphonic)**
Pesticides			**(Phosphonic)**

Notes: A few pesticides are based on the methylphosphonic acid structure. For sarin, $R = i - C_3H_7$ (isopropyl group) and $x = F$. For VX, $R = C_2H_5$ (ethyl group) and $x = SCH_2CH_2N(i - C_3H_7)_2$ (Verweij et al., 1979). Note that the relative volatibilities could be estimates qualitatively based on molecular weights. VX is among the most persistent of the nerve gases, being a thick brown oily liquid. The small X group (a fluorine atom) renders sarin somewhat volatile.

Table 3. Mechanism of the biological action of organophosphorus esters through inhibition of acetyl choline esterase in the nervous systems of higher animals (Fest & Schmidt, 1973; Metcalf, 1982; Gearien, 1982). E signifies the enzyme. The pestide form is shown in channel (B).



(A) $$CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{+}{N}(CH_3)_3 + EH \underset{(1)}{\overset{K_E}{\rightleftharpoons}} CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2\overset{+}{N}(CH_3)_3 \ldots EH \xrightarrow[(2)]{k_1}$$

$$CH_3\overset{\overset{O}{\|}}{C}E + HOCH_2CH_2\overset{+}{N}(CH_3)_3 \xrightarrow[(3)\ H_2O]{k_2} CH_3\overset{\overset{O}{\|}}{C}OH + EH$$

(B) $$(RO)_2\overset{\overset{O}{\|}}{P}X + EH \underset{(1)}{\overset{K_E}{\rightleftharpoons}} (RO)_2\overset{\overset{O}{\|}}{P}X \ldots EH \xrightarrow[(2)]{k_1} (RO)_2\overset{\overset{O}{\|}}{P}E + HX \xrightarrow[(3)\ H_2O]{k_2} (RO)_2\overset{\overset{O}{\|}}{P}OH + EH$$

Table 4. Physical and chemical properties of the nerve agents (Harris et al., 1982).

Property	GA	GB	GD	VX
formula wt	162.13	140.10	182.18	267.38
boiling pt, °C	246	147	167	298
freezing pt, °C	- 50	- 56	unknown	<-51
$d^{25°C}$	1.073	1.0887	1.0222	1.0083
volatility at 25°C, mg/m^3	610	21,900	3,060	10.5

Table 5. Time scales for parathion oxidations in the atmosphere (Woodrow et al., 1983).

Laboratory		Field[a]	
	Half-life (min)	Date	Half-life (min)
Light plus ozone	23	6/04/76	5[b]
Light, no ozone	41	7/23/75	131[c]
Ozone, no light	21,060		
Dark, no ozone	No reaction		

[a] Central Valley of California, USA

[b] At 4:00 p.m.

[c] In the absence of sunlight (9:00 to 10:00 p.m.)

Table 6. Rate constants for gas-phase reactions of OH radicals with a series of organophosphorus compounds at 297K.

k(cm^3 molecule^{-1} second^{-1})

Organophosphorus Compound	$10^{12} \times k_{OH}$
$(CH_3O)_3PO$	7.37 ± 0.74
$(CH_3O)_2P(O)SCH_3$	9.29 ± 0.68
$(CH_3S)_2P(O)OCH_3$	9.59 ± 0.75
$(CH_3O)_3PS$	69.7 ± 3.9
$(CH_3O)_2P(S)SCH_3$	56.0 ± 1.8
$(C_2H_5O)_3PO$	55.3 ± 3.5
$(CH_3O)_2P(O)N(CH_3)_2$	31.9 ± 2.4
$(CH_3O)_2P(S)N(CH_3)_2$	46.8 ± 1.4
$(CH_3O)_2P(S)NHCH_3$	232 ± 13
$(CH_3O)_2P(S)NH_2$	244 ± 9

Table 7. Methane oxidation channels as an example of more general hydrocarbon decay.

$CH_4 + OH \rightarrow CH_3 + H_2O$
$CH_3 + O_2 \rightarrow CH_3O_2$
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$
$CH_3O + O_2 \rightarrow CH_2O + HO_2$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 \rightarrow O_3$
$HO_2 + NO \rightarrow OH + NO_2$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 \rightarrow O_3$

$CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3$

$CH_2O + h\nu \rightarrow CHO + H$
$H + O_2 \rightarrow HO_2$
$CHO + O_2 \rightarrow CO + HO_2$
$HO_2 + NO \rightarrow OH + NO_2$
$HO_2 + NO \rightarrow OH + NO_2$
$NO_2 + h\nu \rightarrow NO + O$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 \rightarrow O_3$
$O + O_2 \rightarrow O_3$

$CH_2O + 4O_2 \rightarrow CO + 2OH + 2O_3$

$CH_2O + OH \rightarrow CHO + H_2O$
$CHO + O_2 \rightarrow CO + HO_2$
$HO_2 + NO \rightarrow OH + NO_2$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 \rightarrow O_3$

$CH_2O + 2O_2 \rightarrow CO + H_2O + O_3$

$CO + OH \rightarrow CO_2 + H$
$H + O_2 \rightarrow HO_2$
$HO_2 + NO \rightarrow OH + NO_2$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 \rightarrow O_3$

$CO + 2O_2 \rightarrow CO_2 + O_3$

Table 8. Midday concentrations of major pollutants in the urban photochemistry and aerosol systems for a first world and developing megacity.

	Los Angeles	Mexico City
NO_x	100 ppb	250 ppb
NMHC	1000 ppbC	2000 ppbC
O_3	150 ppb	300 ppb
OH	10^6 to $\geq 10^7$ cm^{-3}	10^6 to $\geq 10^7$ cm^{-3}
RSP	100 $\mu g\ m^{-3}$	200 $\mu g\ m^{-3}$
.01 to 0.1 μ	10^5 to 10^6 cm^{-3}	$2 \times 10^5 - 2 \times 10^6$ cm^{-3}
0.1 to 1 μ	3×10^3 cm^{-3}	6×10^3 cm^{-3}

Table 9. Partial (per hydrogen) abstraction rate constants for the attack of hydroxyl radical on organic molecules with different substituents X.

	X Group					
	ONO_2[a]	H[b]	CH_3[c]	OH[d]	OCH_3[e]	$OP(O)(OCH_3)_2$[f]
$HC\underline{H}_2$-X	0.01	[.002]	0.05	0.3	0.5	0.6
$RC\underline{H}_2$-X	0.01	0.05[g]	0.50[h]	1.2[i]		
$R_2C\underline{H}$-X	0.13	0.50[h]	2.0[j]	5.0[k]		
$C\underline{H}_3$CHX-R	0.02	0.05[g,h]	0.05[g,h]			
$C\underline{H}_3CH_2$CHX-R	0.08					

a. Data from Gaffney et al. 1986.
b. Methane anomalous, so in brackets.
a-e. All rate constants from Atkinson 1986) unless otherwise stated.
d. We assume abstraction of the alcoholic hydrogen is slow (Demore et al. 1990).
f. Winer and Atkinson (1990).
g. Estimated from ethane and 2, 2, 3, 3 tetramethyl butane.
h. Estimated from propane and 2, 2, 3, 3 tetramethyl butane.
i. Estimated from ethanol.
j. Estimated from $CH(CH_3)_3$.
k. Estimated from 2 propanol.

Table 10. Dissociation constants ($K_a \times 10^5$) for benzoic acid derivatives.

	H	CH_3	OCH_3	F	Cl	NO_2
o (ortho)	6	12	8	54	114	671
m (meta)	6	5	8	14	15	32
p (para)	6	4	3	7	11	37

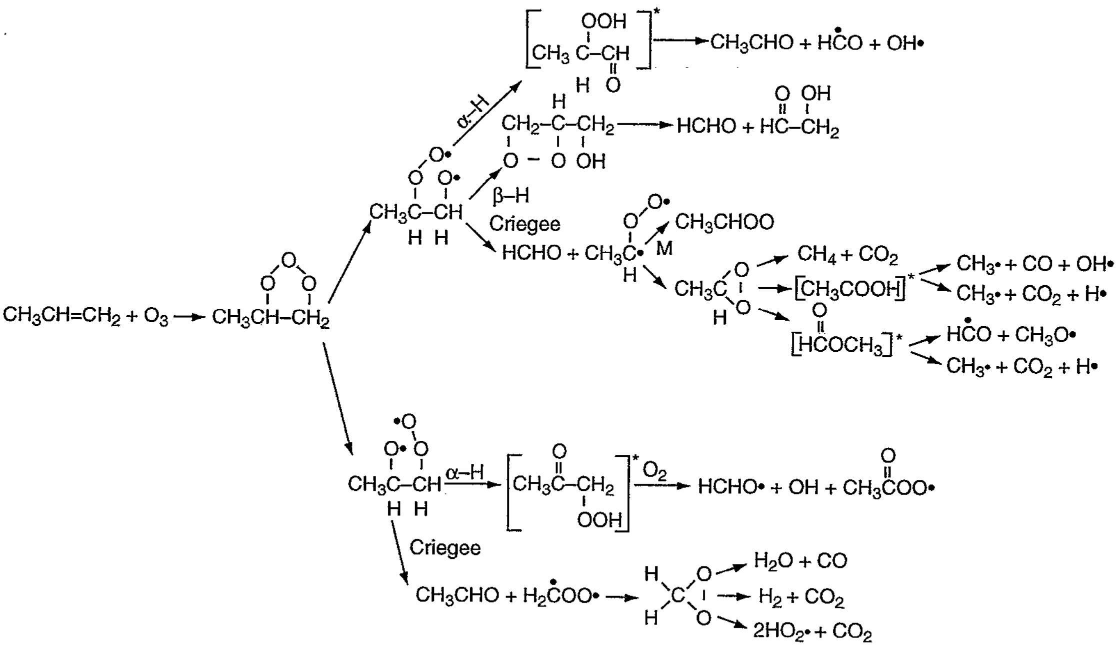


Figure 1. Propylene decay through ozone reaction in the mechanism of Falls and Seinfeld (1978). An analogous chain exists for hydroxyl attack.

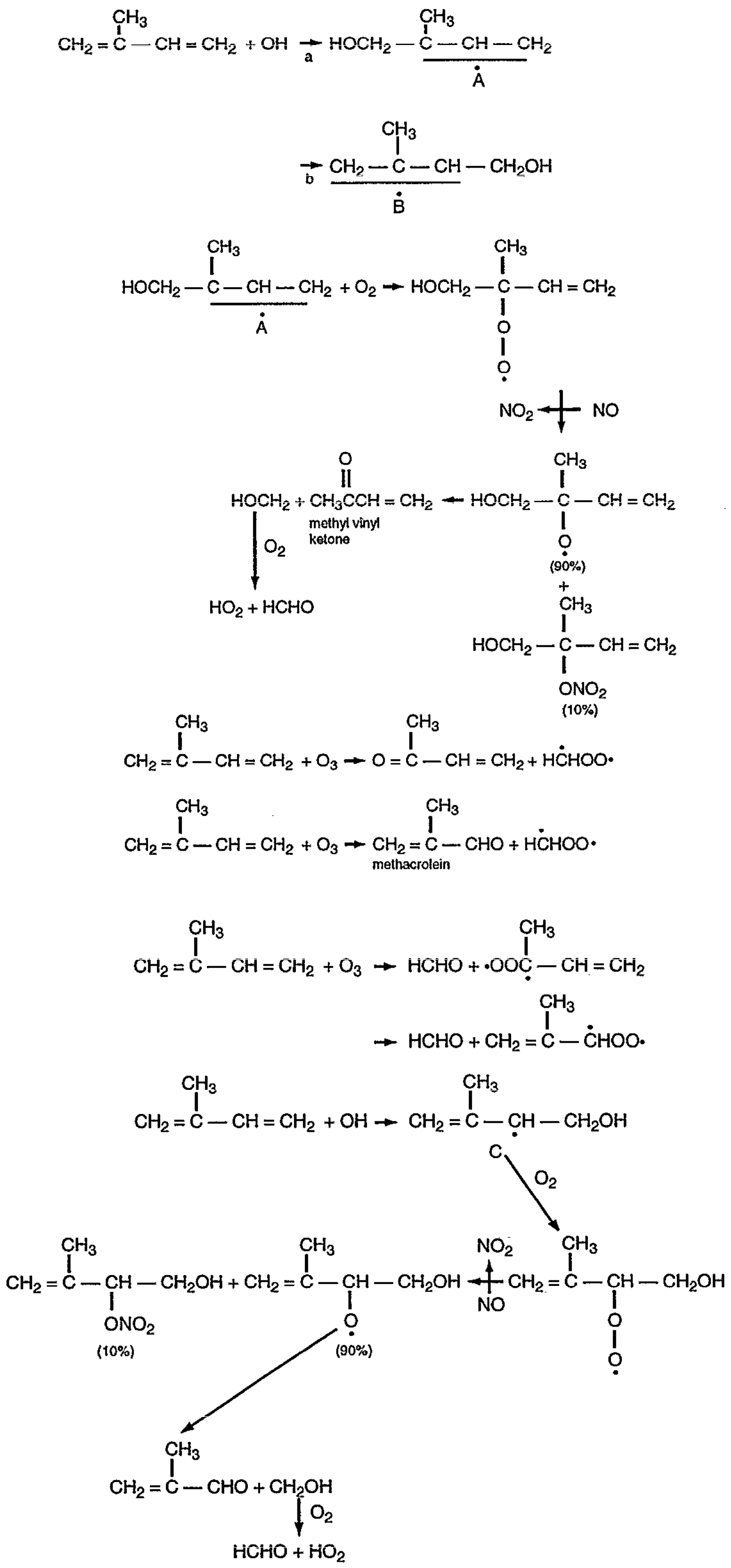


Figure 2. An idealized isoprene decay set for nonurban tropospheric conditions (Niki et al. 1983; Gu et al., 1985; Lloyd et al., 1983).

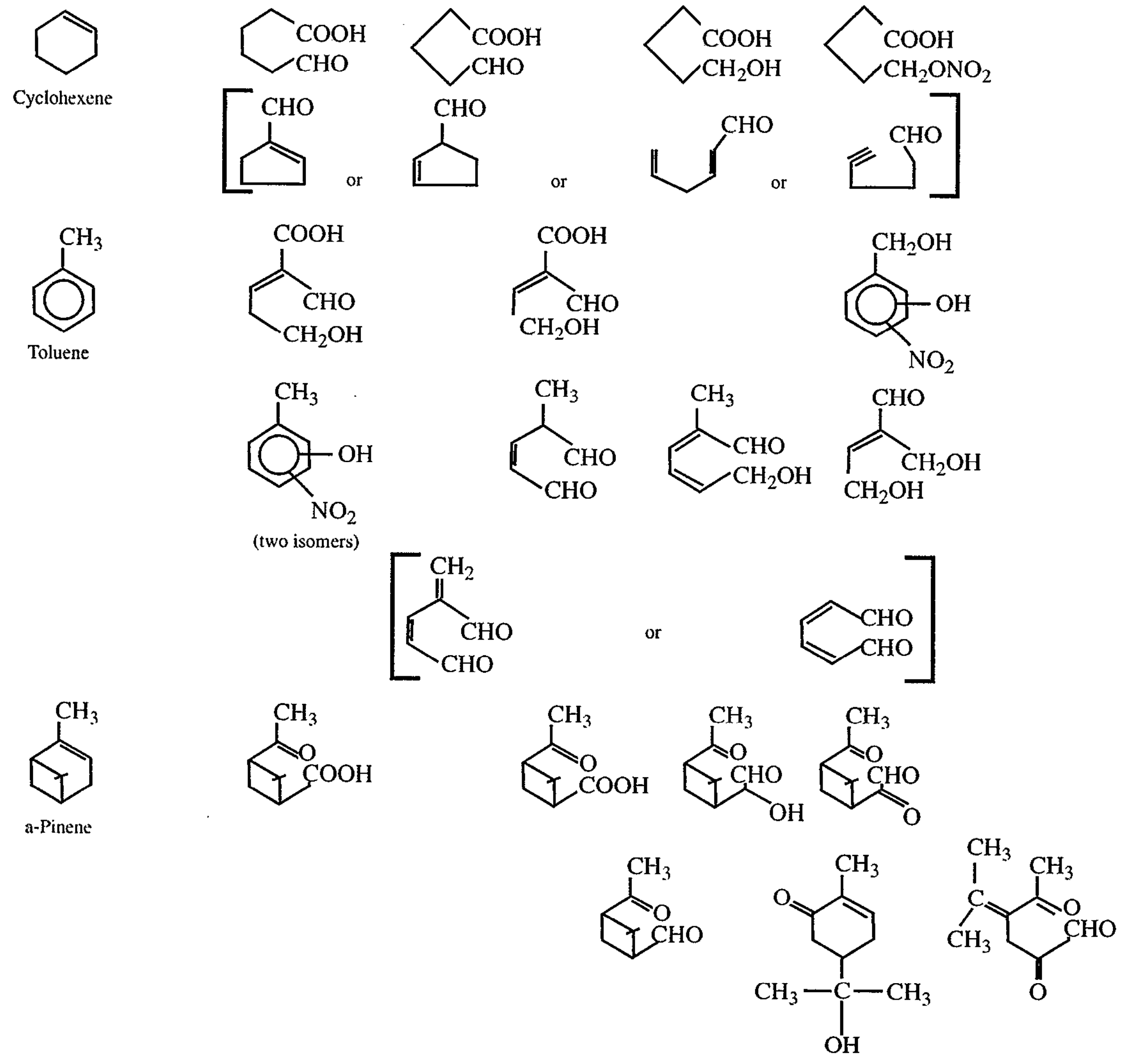
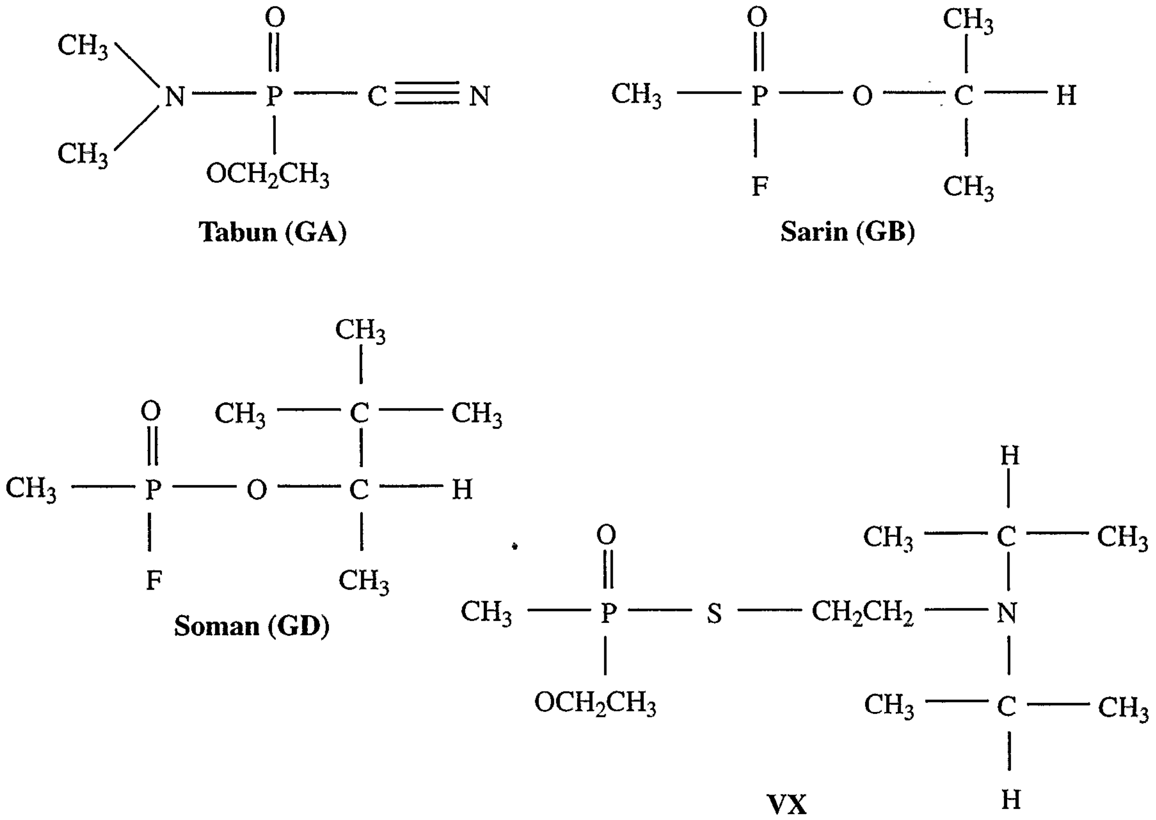


Figure 3. Particle phase products likely to result from photochemical decay of some cyclic organics in the urban atmosphere (Schwartz, 1974).



Tabun (GA)

Sarin (GB)

Soman (GD)

VX

Figure 4. Chemical structures of sarin and some related nerve agents (Dept. of Commerce, 1994).

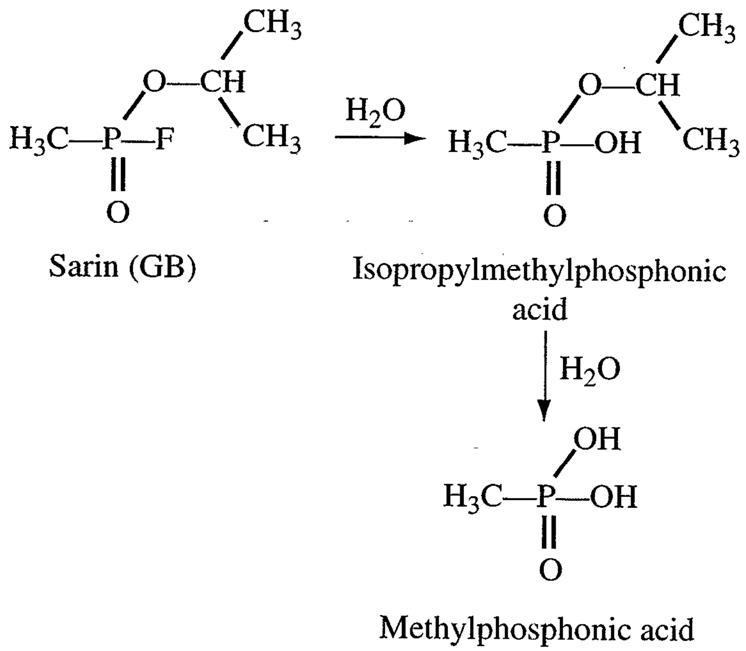
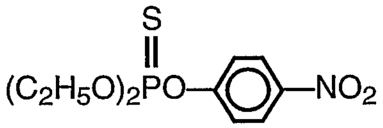
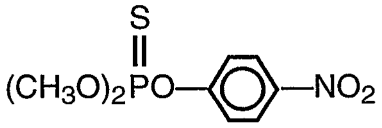


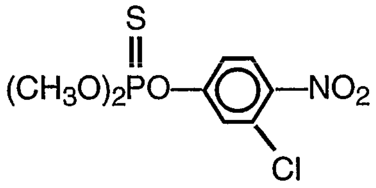
Figure 5. Generalized sarin hydrolysis sequence.



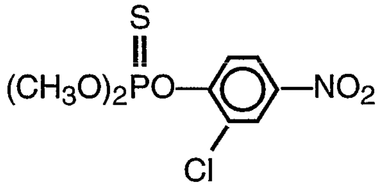
Parathion



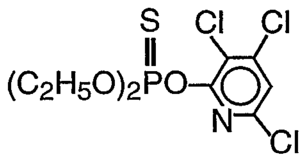
Methyl Parathion



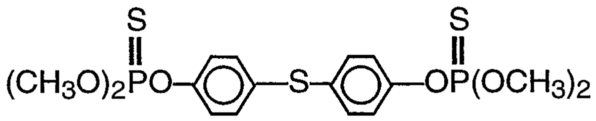
Chlorthion



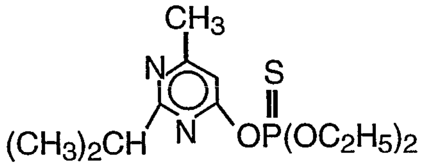
Dicapthon



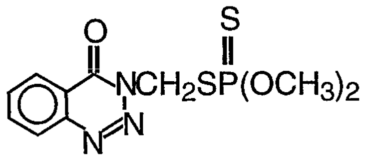
Chlorpyrifos



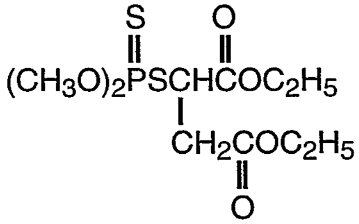
Temephos



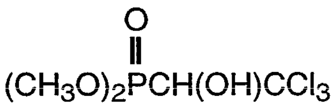
Diazinon



Azinphosmethyl



Malathion



$(CH_3O)_2\overset{O}{\overset{\|}{P}}CH(OH)CCl_3$

Trichlorfon

Figure 6. Structures of some typical organophosphorus pesticides (Metcalf, 1982 and O'Brien, 1960).

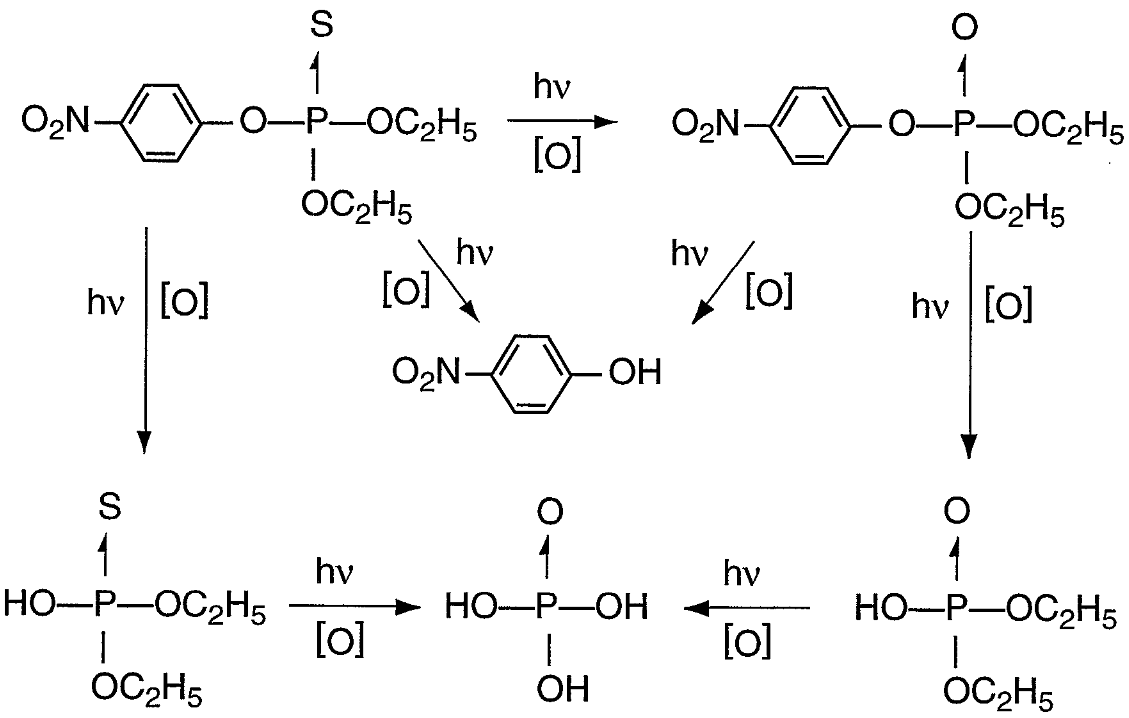


Figure 7. A schematic of daytime atmospheric parathion oxidation (Woodrow et al., 1983). The phosphorus double bond is represented by a single-barbed arrow.

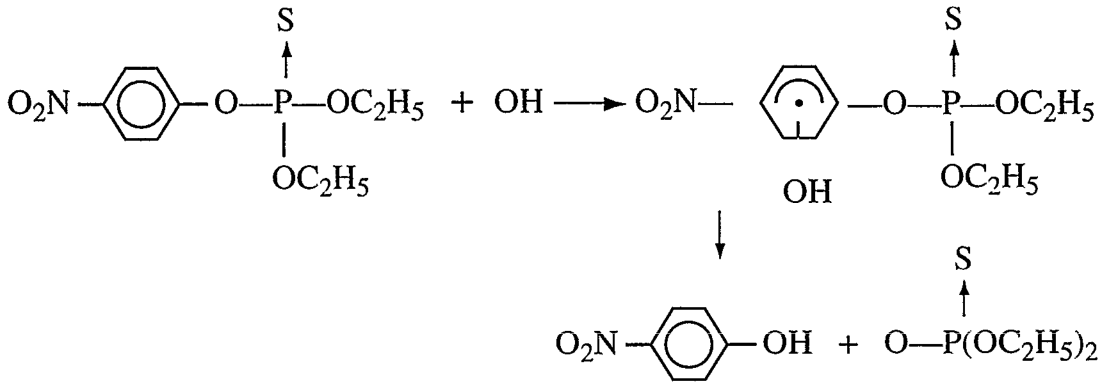


Figure 8. Hydroxl radical attack on parathion may eject p-nitrophenol (Woodrow et al., 1977 and Finlayson Pitts and Pitts, 1986). Here the phosphorus double bond is a double-barbed arrow.

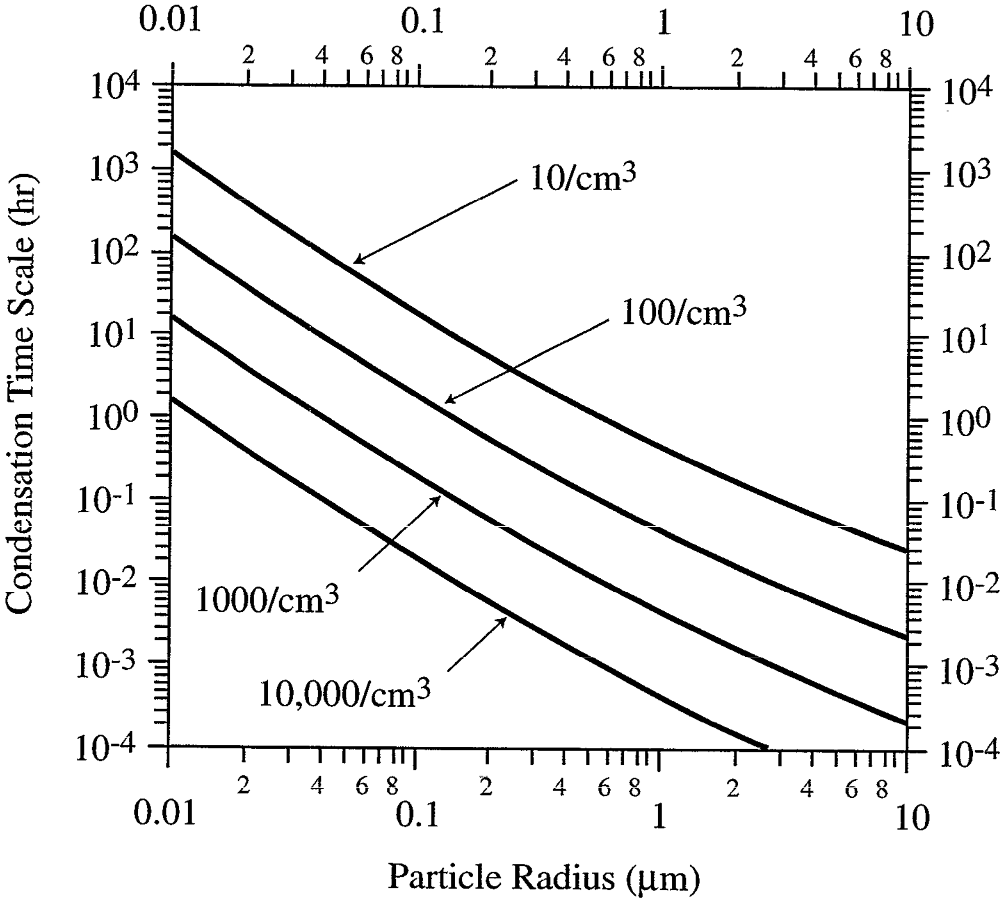


Figure 9. Characteristic time for removal of vapor to particle as a function of radius and aerosol number concentration.

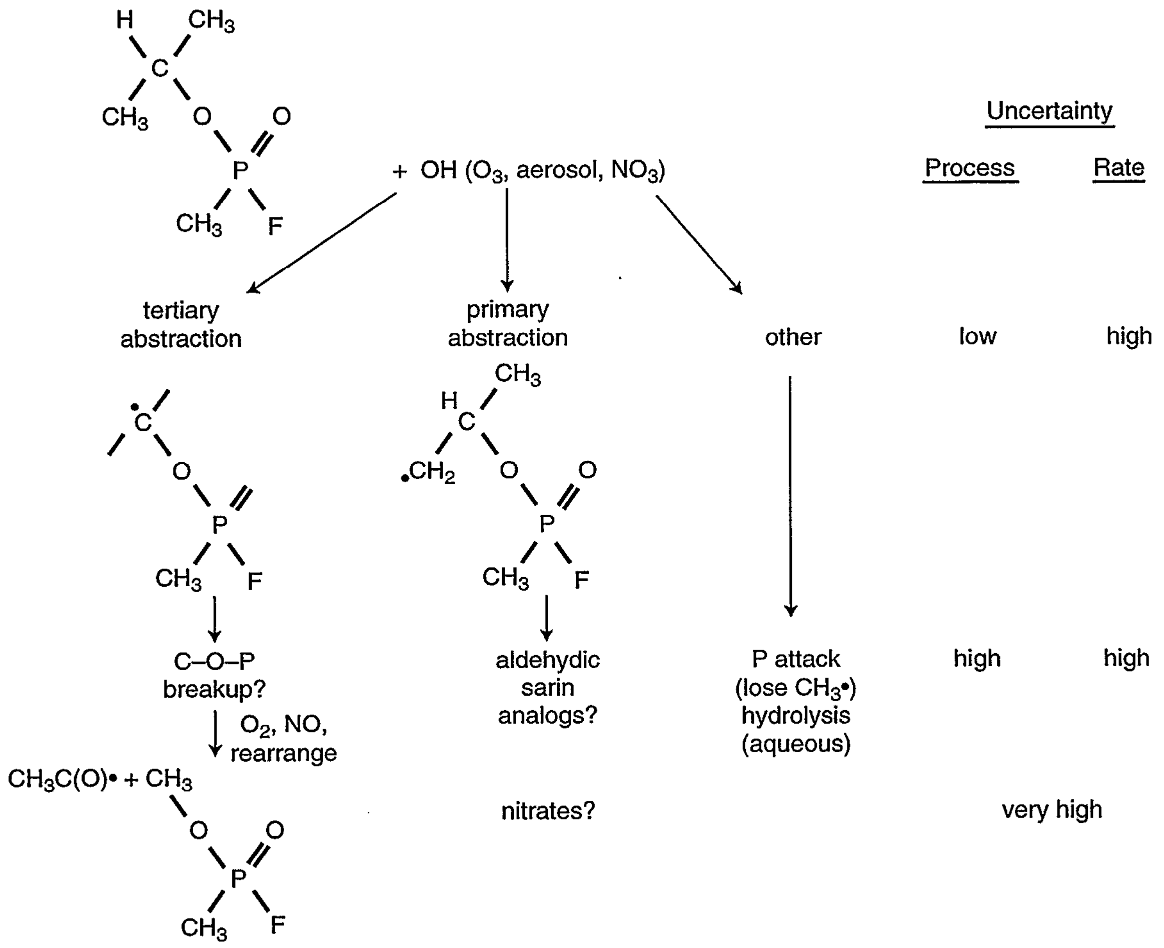


Figure 10. The sarin structure, urban reaction partners presented schematically, and potential degradation pathways. Right hand columns indicate in a qualitative sense the uncertainties inherent in the existence of the processes and their rates at various levels in the diagram.

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