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The Role of Heterogeneity in the Kinetics of a Surface Reaction

I. Infrared Characterization of the Adsorption Structures of Organophosphonates and Their Decomposition[1]

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Infrared investigation shows that isopropyl methylphosphonofluoridate (sarin) is strongly adsorbed on γ-alumina via its phosphoryl oxygen. Two decomposition reactions are observed: either propene is liberated as a result of dealkylation of the adsorbed species or the P–F bond is hydrolyzed. Fluorine released in the latter reaction is also adsorbed; the remaining phosphorus compound is bonded to the surface via its POO grouping. The hydrolysis reaction, which is the predominant process, is activated by basic surface sites. Water accelerates this reaction. The surface is inactivated by adsorption of HF. The hydrolysis proceeds considerably faster over magnesium oxide.

INTRODUCTION

Our laboratory is occupied in the research and development of means and methods to protect human beings in a toxic environment (*1*). Part of the research is directed towards the purification of air which is contaminated with noxious compounds that are potential chemical warfare agents.

The organophosphorus compounds capable of enzyme inhibition constitute the most threatening group of warfare agents. The pharmacological activity of these "nerve agents" is described in detail in the literature (*2*). In man and animals these gases are operative through inactivation of the enzyme cholinesterase. This enzyme effects the fission of acetylcholine, which is the chemical transmitter of a stimulus between nerve cells (*3*). If acetylcholine is no longer decomposed the receiving nerve and muscle cells are continuously stimulated. This disturbance of the neural transmission finally leads to the death of the victim.

Charcoal filters, widely applied in gasmasks and large filter installations to purify contaminated air, adsorb nerve gases physically. The adsorption is strong but reversible. Therefore, it is desirable to decompose the agent when adsorbed. During World War II an impregnation of the charcoal adsorbent was developed which made it possible to chemisorb and hydrolyze agents like hydrogen cyanide and cyanogen chloride (*4*). The material impregnated is a mixture of copper, chromium and silver salts. Smišek and Černý (*5*) mentioned a number of chemical effects upon warfare agents induced by inorganic impregnations. Most of these chemical interactions between adsorbent and agent involve a surface reaction, consuming the impregnation material. A few others are catalytic, decomposing the toxic agent into less harmful volatile compounds. A cata-

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[1] This work is part of a thesis by A. E. T. K., Eindhoven, 1974.

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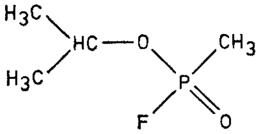
lytic process is generally to be preferred because a limited amount of catalytic material is essentially able to convert large quantities of toxic vapor. The realization of a catalyst in the proper sense, however, is at present extremely difficult. The unsettled problems concern not only the activity, but also the poisoning of the catalyst.

It seems easier to select a decontaminating adsorbent. Such an adsorbent has two functions: it adsorbs the agent and decomposes it subsequently. It differs from a catalyst in that at least one of the reaction products remains adsorbed, thus destroying the activity to decontamination.

Since a broad variety of agents has to be covered a general type of decomposition reaction needs to be chosen. Two possibilities enter the picture, viz, hydrolysis and oxidation. For both types of reaction the additional required reactant, water or oxygen, is profusely present in the ambient air. At room temperature hydrolysis proceeds faster than oxidation, which makes the former seem the more promising type of reaction with respect to decontaminating adsorbents.

In the present study the hydrolysis of adsorbed organophosphorus compounds is investigated. Attention is directed towards one definite adsorbate–adsorbent system, namely, isopropyl methylphosphonofluoridate (IMPF or "sarin") on γ-alumina:



Sarin is chosen as a representative organophosphorus warfare agent, whereas γ-alumina is taken as adsorbent because its chemical and physical surface properties have been studied extensively. Qualitative results are available from an infrared investigation of the adsorbed species (*6*) and is discussed here in a somewhat condensed form. The decomposition of adsorbed sarin has been studied quantitatively using a microcalorimeter. The results obtained with this instrument are described in the next paper (*29*).

METHODS

Adsorbents

Most infrared experiments have been performed with a commercial alumina, known as type C from Degussa (Frankfurt, Germany). This material was heated at 750°C in air for about 16 hr. An X-ray diffractogram revealed that after this pretreatment most of the material was γ-alumina; however, some δ-alumina was also present. The surface area was 120 m^2/g. Approximately 45 mg of this material was pressed in a 1.125 in. die at a pressure of 2 ton/cm^2 into a self-supporting disk. To prevent sticking of the disk to the die the alumina powder was pressed between two pieces of filter paper. Afterwards the paper was burned off by heating the disk in air at 750°C. The surface area of the resulting sample was about 110 m^2/g.

The magnesium oxide used in some experiments was prepared according to Baird and Lunsford (*7*). With a final pretreatment temperature of 400°C a surface area of 180 m^2/g was obtained. From this material small particles (<5 μm) were separated by sedimentation following a procedure described by Hunt *et al.* (*8*). It was not necessary to use filter papers when pressing self-supporting disks from this powder.

One experiment has been performed with a pure γ-alumina made available by Ketjen (AKZO Chemie Nederland, Amsterdam, The Netherlands). The surface area of this product was 280 m^2/g. For infrared investigation the material was processed similarly to magnesium oxide.

The properties of both Degussa and Ketjen alumina have been described before (*9, 10*).

Adsorbates

The organophosphorus compounds used were synthesized by the department of

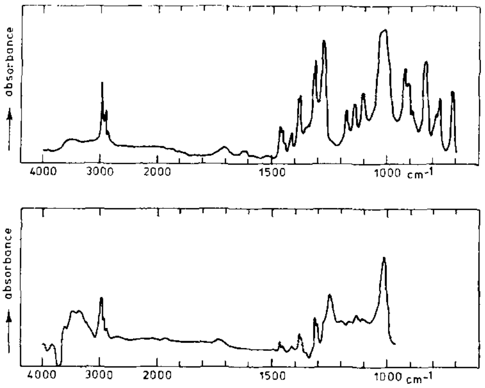


FIG. 1. Infrared spectrum of sarin (top) and sarin adsorbed on γ-alumina (bottom).

organic chemistry of this laboratory according to standard procedures [see e.g., Ref. (*11*)]. Hydrogen fluoride was obtained from Union Carbide in a high pressure cylinder and used without further purification.

Apparatus

The spectra of the organophosphorus compounds in the liquid phase were recorded at standard conditions on a Grubb-Parsons "Spectromajor." Infrared spectra of adsorbed molecules were recorded on a Cary-White Model 90 double beam spectrophotometer. This model is a dual frequency ratio recording, prism-grating instrument. The reference signal is held constant by automatic gain control. The following operation conditions of the spectrometer were selected:

slit width	5 cm^{-1} over the whole range from 4000–450 cm^{-1}
scanning speed	1 cm^{-1}/sec
pen period	30 sec (time constant ~5 sec)
ordinate scale	extinction: 0–1.0.

The recorder signal was fed to a Digiac computer. In every 2.5 cm^{-1} scan the signal was sampled 16 times and the computed mean value was punched on tape. Thus a spectrum of 4000–1000 cm^{-1} was converted into 1200 numbers, which could be stored in the memory of the computer for processing.

Two identical Pyrex cells, one placed in the sample beam and the other in the reference beam, were used. Both cells could be heated to 400°C and were connected to a vacuum line, thus permitting spectra of adsorbed molecules to be recorded *in situ*. Experiments that required higher pretreatment temperatures were performed in quartz cells.

Procedure

Prior to adsorption the adsorbents were evacuated *in situ* at room temperature for 20 hr (10^{-4} Torr). After this treatment a background spectrum was recorded. Adsorbates were introduced into the sample cell via the vapor phase at a pressure of a few Torr. Spectra of adsorbed molecules were recorded after removal of the vapor. To avoid adsorption of volatile components of the vacuum grease the valves and joints of the vacuum system were subjected to a prolonged heat and vacuum treatment.

RESULTS

Adsorption Structures

A rough survey of the alterations in the infrared spectrum of sarin caused by adsorption on γ-alumina, may be obtained from Fig. 1 or Table 1. The assignments of the absorptions of the pure liquid, as given in Table 1, have been based on a vibrational study of sarin published before (*6*). No spectroscopic information about the adsorbed species is available at frequencies smaller than 1000 cm^{-1} because of the insufficient transparency of the alumina disks in this region.

Figure 1 shows that adsorption has not induced appreciable changes with regard to the C–H stretchings and deformations. The absorption of the ν[C–O–(P)] has not shifted either; however, its band contour seems narrower. Substantial alterations are observed in two regions of the spectrum, viz, 1300–1000 cm^{-1} and 4000–3000 cm^{-1}. In the latter region absorption due to O–H vibrations occurs, originating from hydroxyl groups and water molecules adsorbed on the alumina surface. The "negative peak" at 3700 cm^{-1} indicates the disappearance of certain hydroxyl groups from the sample disk. Instead other oxygen–hydrogen structures have developed that absorb at frequencies between 3600 and 3000 cm^{-1}. As the 1300–1000 cm^{-1} region will yield more direct information about the adsorption, this paper focuses mainly on the interpretation of the spectroscopic features observed in this frequency range.

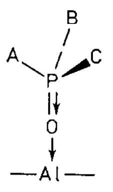
The frequency (wavenumber) of the $\nu(P{=}O)$ absorption is found to be reduced by approximately 30 cm^{-1}, being positioned at 1245 cm^{-1}. This may be explained in two ways: (a) on γ-alumina sarin is adsorbed via its P=O group or (b) via the P–F group, causing a decrease of the electronegativity of the fluorine substituent and thus a shift of the phosphoryl frequency to a smaller value (*12*). It is possible to discriminate between the two possibilities by studying the adsorption of a series of sarin derivatives (*6*). Infrared data on the more important compounds of this series are summarized in Table 2. It appears that the presence of fluorine is not necessary to observe a spectral change as for sarin. Also the infrared spectrum of adsorbed diisopropyl methylphosphonate (DIMP) shows a shift of $\nu(P{=}O)$ of about 30 cm^{-1} compared to the pure liquid. The infrared bands in the 1260–1200 cm^{-1} region (Table 2) are therefore related to adsorbed structures in which the P=O is linked to the alumina surface. It is very likely that the adsorption takes place on an acid surface site. Two structures may be proposed:

TABLE 1

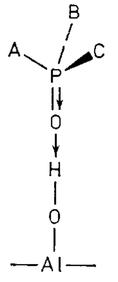
Infrared Absorption Frequencies of Pure and Adsorbed Sarin (cm^{-1})[a]

Liquid	Adsorbed	Assignment
2985 s	2980 s	$\nu_{as}CH_3$
2932 m	2930 m	$\nu_{s}CH_3$
2878 w	2870 w	νCH
1724 w	1730 w	721 + 1014 = 1735
1468 m	1465 mw	$\delta_{as}CH_3$(ipr)
1461 m	1455 mw	
1419 w	1415 w	$\delta_{as}CH_3$(me)
1390 m	1380 m	$\delta_{s}CH_3$(ipr)
1380 m		
1351 w	1350 w	δCH
1320 s	1320 s	$\delta_{s}CH_3$(me)
	1315 s	
1277 vs	1245 s	$\nu P{=}O$
1180 m	1170 w	CH_3(ipr)rock
1145 m	1135 m	
1106 m	1110 m	
1014 vs	1020 vs	$\nu C\text{–}O\text{–}(P)$
921 s		CH_3(me)rock
905 s		
884 sh		$\nu_{s}C\text{–}C\text{–}C$
835 s		$\nu P\text{–}F$
778 ms		$\nu P\text{–}C$
721 ms		$\nu P\text{–}O\text{–}(C)$

[a] m, s, sh, v, w denote medium, strong, shoulder, very, weak, respectively.



(I)



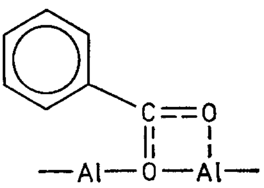
(I′)

The P=O group of structure **I′** is perturbed by hydrogen bonding, which causes the phosphoryl frequency to shift downscale (*13*). The O–H vibration of the hydroxyl group is also affected, which explains both the negative 3700 cm^{-1} band and the broad absorption between 3600 and 3000 cm^{-1}.

On the other hand, the phosphoryl p_π–d_π back-bonding in structure **I** is reduced upon adsorption, resulting in a decreased P=O bond order which may equally well account for the observed shift of the $\nu(P{=}O)$. A sarin molecule that has been adsorbed according to structure **I** must have driven away a hydroxyl group from an aluminum ion. This hydroxyl group may be readsorbed on the surface, which explains both the negative 3700 $\mathrm{cm^{-1}}$ band and the broad absorption between 3600 and 3000 $\mathrm{cm^{-1}}$.

Although the spectroscopic evidence presented so far does not allow us to discriminate between the two possibilities, for two reasons structure **I** is preferred:

1. Sarin adsorbs just as well on an alumina sample that has been pretreated *in vacuo* at 900°C. From the results of a study of γ-alumina (*9*), it is known that almost all hydroxyl groups have disappeared from the surface at that temperature. Nevertheless a very similar spectrum was observed upon adsorption of sarin.
2. When benzaldehyde is adsorbed on the same γ-alumina the changes observed in the hydroxyl stretching region of the infrared spectrum are identical to those noticed upon the adsorption of sarin (*10*). It has been shown that the structure of adsorbed benzaldehyde is



which implies that hydroxyl groups must have been driven away from aluminum atoms in the surface layer of the adsorbent.

However, the situation at the surface is more complex than is represented by structure **I** only. A closer look at the infrared spectrum of adsorbed sarin (Fig. 2) reveals that the intensities of the absorption between 1300 and 1000 $\mathrm{cm^{-1}}$ gradually change with time. Simultaneously with a decrease of the intensity of the band at 1245 $\mathrm{cm^{-1}}$ the intensity of the absorption around 1120 $\mathrm{cm^{-1}}$ increases, whereas the 1020 $\mathrm{cm^{-1}}$ band is narrowed. This suggests the existence of another adsorption structure, which is gradually formed from structure **I**. Similar indication may be obtained from Table 2; compounds showing a strong band in the 1260–1200 $\mathrm{cm^{-1}}$ region of the spectrum when adsorbed, invariably display weak bands between 1200 and 1160 $\mathrm{cm^{-1}}$ and between 1120 and 1060 $\mathrm{cm^{-1}}$. It is noteworthy that the spectra of compounds without fluorine show a very strong 1260–1200 $\mathrm{cm^{-1}}$ band upon adsorption, which does not change with time.

Another indication that the P–F bond is involved in the surface reaction observed in the infrared spectrum of adsorbed sarin is derived from the effect of water vapor. When water vapor is added the spectrum shown in Fig. 3 is obtained after evacuation. The 1245 $\mathrm{cm^{-1}}$ phosphoryl absorption has almost completely disappeared and instead a broad and very intense band, centered around 1120 $\mathrm{cm^{-1}}$, is observed. The C–O–(P) absorption has shifted to a slightly lower wavenumber (1010 $\mathrm{cm^{-1}}$). After 20 hr of alternating water dosing and evacuation the intensities of both the 1120 and 1010 $\mathrm{cm^{-1}}$ absorption have reached a maximum. The most plausible reaction that can account for these observations is the hydrolysis of the P–F bond, resulting in the formation of HF:

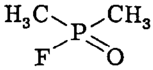
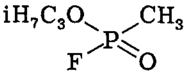
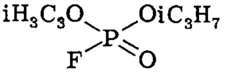
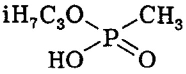
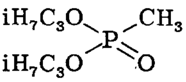
$$\mathrm{P^V{-}F} + \mathrm{H_2O} \rightarrow \mathrm{P^V{-}OH} + \mathrm{HF}.$$

Neither mass spectra nor infrared spectra of the vapor phase have offered any evidence for the presence of HF. If HF is formed the implication is that it is adsorbed on the alumina surface. For this reason in an independent experiment hydrogen fluoride was admitted to an alumina disk and the infrared spectrum was recorded after evacuation of the vapor (Fig. 4).

It appears that HF is very well adsorbed on γ-alumina, giving rise to a broad and intense absorption at 1120 $\mathrm{cm^{-1}}$ and a weak but also broad band around 1660 $\mathrm{cm^{-1}}$. The 1120 $\mathrm{cm^{-1}}$ band coincides with

TABLE 2

Infrared Absorptions between 1300–1000 cm^{-1} of Some Sarin Derivatives Adsorbed on Alumina[a]

Compound		$\nu P{=}O_{ads}$ (shift)		$\nu C{-}O{-}(P)_{ads}$
	DMPF	—	1160 s 1085 s	—
	IMPF "sarin"	1245 s (−32)	1170 w 1135 m 1110 m	1020 vs
	DFP	1260 s (−35)	1160 w 1135 ms 1085 ms	1010 vs
	IMPA "hydroxysarin"	—	1180 s 1140 s 1090 s	1005 vs
	DIMP	1212 s (−29)	1185 sh 1145 w 1110 m	1010 vs

[a] (shift) = difference in wavenumber with $\nu P{=}O$ of corresponding pure liquid.

the maximum of the absorption in the spectrum of Fig. 3, which may, therefore, be explained by HF formation and adsorption. The remaining phosphorus compound must then be very similar to adsorbed hydroxysarin, which is also characterized by intense absorption between 1180 and 1090 cm^{-1} (see Fig. 5 and Table 2).

It is more difficult to identify the structure of hydrolyzed adsorbed sarin (structure II) from the infrared spectrum, because of overlap of its specific bands with the absorptions of the rocking modes of the isopropyl group and with the 1120 cm^{-1} band. The most satisfying assignment is arrived at when it is recognized that structure II is characterized by two strong bands, at about 1180 and 1080 cm^{-1}, respectively. This may be derived from Table 2 and can be illustrated with Figs. 5 and 6. In the spectrum of adsorbed hydroxysarin the isopropyl rockings are observed at 1180, 1140 and 1110 cm^{-1}, on top of a strong and broad absorption centered at about 1180 cm^{-1}; in addition, a strong band is observed at 1090 cm^{-1}. In the spectrum of adsorbed dimethyl phosphinoic fluoride (DMPF) (Fig. 6) two

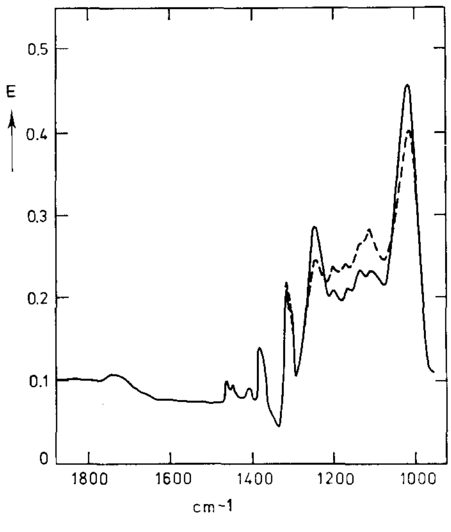


FIG. 2. Sarin/Al$_2$O$_3$. (——) spectrum after 5 hr.

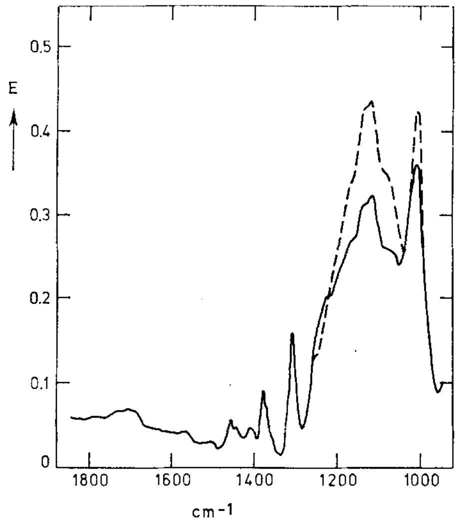


FIG. 3. Sarin/Al_2O_3 after addition of water. (— —) spectrum after 20 hr.

strong bands dominate, at 1160 and 1085 cm^{-1}, respectively. Although this compound is known to be highly reactive towards water (*14*, *15*) no changes can be observed when water is added to the sample characterized by the spectrum shown in Fig. 6. Moreover, no infrared absorption at a wavenumber that is about 30 cm^{-1} smaller than that of the phosphoryl stretching of the liquid is perceptible. Obviously, the compound is immediately hydrolyzed upon adsorption, which is also reflected in its infrared spectrum by the shoulder, due to adsorbed fluoride, in between the two strong bands belonging to a structure **II**.

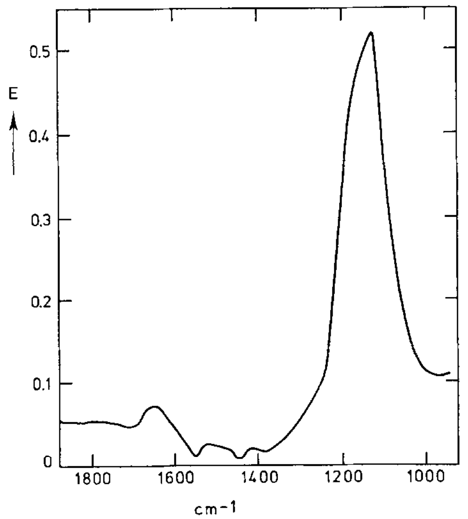
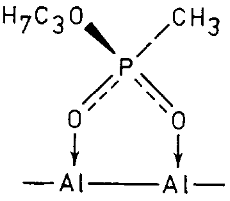


FIG. 4. Hydrogen fluoride/Al_2O_3.

In view of the fact that hydrolysis causes the phosphoryl band at 1245 cm^{-1} to disappear, which may be interpreted in terms of a further reduction of the P=O bond order, we propose to assign the two strong bands in the 1200–1060 cm^{-1} region to the $\nu_s(\mathrm{P}\begin{array}{l}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{array})$ and $\nu_{as}(\mathrm{P}\begin{array}{l}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{array})$ vibrations of the following structure:



(II)

The two equivalent P–O bonds in structure **II** may be expected to be very similar to those in ionized phosphorus compounds and metal phosphonato complexes. An impression of the absorption frequencies of such POO stretchings may be obtained from literature data of compounds comparable to structure **II** (*16–21*). The intensities of the two POO bands are reported to be strong; their frequency depends on the substituents on phosphorus as well as on the cation (*22*), but the bands are always found within the overall frequency range of 1300–1000 cm^{-1}. The two stretching modes are separated by 100 cm^{-1}, approximately.

The absorptions in the 1200–1050 cm^{-1} region observed for the adsorbed compound (Table 2) concur very well with these literature data. Relatively small deviations may be due to several causes: (a) the structure which exists at the alumina surface is not quite the same as a salt or a metal complex; (b) the bands of the rocking mode of the isopropyl group overlap the POO absorptions.

The Al–O bonds in structure **II** are expected to absorb at wavenumbers lower than 1000 cm^{-1} and hence cannot be observed.

The stability of adsorption complex **II** might be comparable to that of metal phosphonato complexes, which would imply that a fairly strong adsorption is formed. Indeed, the intensity of the bands in the spectrum of adsorbed DMPF does not diminish at all when the sample is heated *in vacuo* to 350°C, whereas only small frequency shifts are observed at that temperature.

One experiment was performed with Ketjen alumina samples. It is very difficult to press self-supporting disks from this material that have sufficient transparency in the infrared. We succeeded in pressing pellets that were transparent down to 1200 cm^{-1}. The surface area of this alumina is more than twice as large as that of the Degussa product, which favors the observation of infrared bands due to adsorbed species. Sarin appeared to adsorb very well on this sample, showing intense bands at 1380, 1320, and 1245 cm^{-1}. The ratio in intensity between the 1320 and 1245 cm^{-1} absorptions was about the same as observed shortly after adsorption on Degussa alumina. The intensity of the 1245 cm^{-1} band decreased slowly; when water vapor was admitted this band disappeared rapidly. From this it may be concluded that Ketjen and Degussa alumina behave similarly to the adsorption and decomposition of sarin.

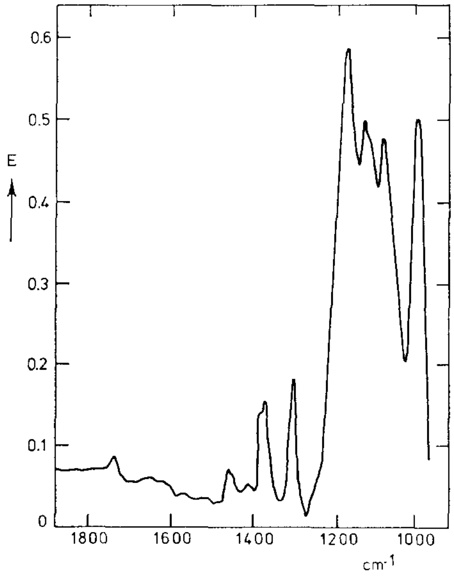


FIG. 5. Hydroxysarin/Al_2O_3.

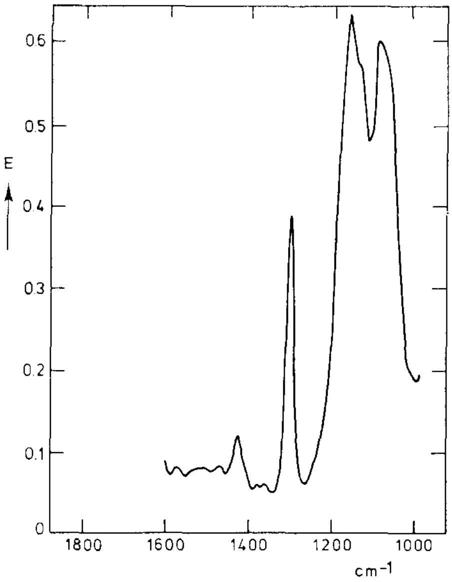
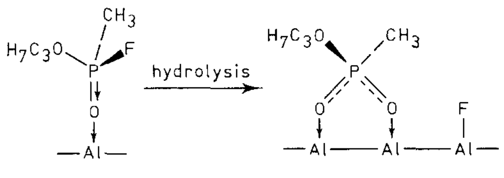


FIG. 6. Dimethyl phosphinoic fluoride (DMPF)/Al_2O_3.

Hydrolysis of Adsorbed Sarin

The spectroscopic evidence presented so far allows us to represent the surface reaction of adsorbed sarin as:



In order to determine the nature of the surface sites involved in this hydrolysis reaction, a series of experiments using various adsorbents has been carried out.

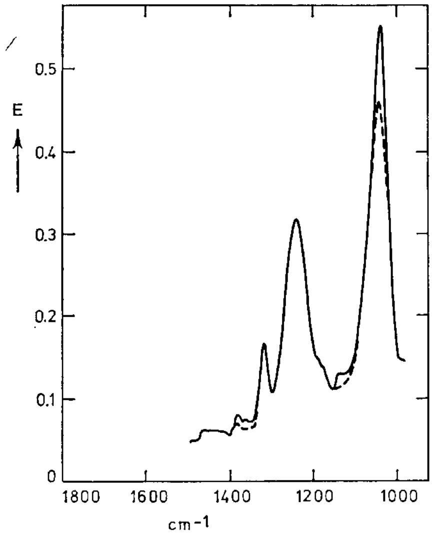


FIG. 7. Sarin/Al_2O_3–HF.

A. Prior to the adsorption of sarin, hydrogen fluoride was admitted to the sample cell and allowed to adsorb on the alumina disk for about 10 min. An intense band, centered at 1120 cm^{-1}, proved that a large quantity of HF was adsorbed. The HF infrared band was compensated for by a subsequent admission of HF to the reference cell. Thus a straight base line was attained. Then sarin was admitted to the sample disk. After evacuation the spectrum shown in Fig. 7 was recorded. Two strong bands dominate, at 1240 and 1040 cm^{-1}. Evidently only structure **I** has developed. After 1000 min of continuous evacuation the spectrum indicated by the broken line is obtained. Some dealkylation (see below) has occurred (decreased intensities of the 1040, 1140, and 1380 cm^{-1} bands); however, not the slightest indication of hydrolysis can be found. Even addition of water vapor is unable to induce any conversion into structure **II**.

Two conclusions may be drawn from this experiment:

1. HF adsorbed prior to sarin on alumina, inhibits the hydrolysis, but not the adsorption of sarin.
2. The ν[C–O–(P)] vibration of structure **I** is found in the range of 1040–1020 cm^{-1}.

Figure 3 shows that after addition of water to adsorbed sarin the ν[C–O–(P)] vibration is observed at 1010 cm^{-1} (structure **II**). Thus the "narrowing" influence on the C–O–(P) band contour, noticed when water is admitted, can be explained.

B. An experiment similar to A was performed with DMPF instead of sarin. The pre-adsorbed hydrogen fluoride proved to exert a marked influence on the spectrum: no bands could be observed between 1200 and 1000 cm^{-1}, whereas a strong band appeared at 1225 cm^{-1} (Fig. 8). Obviously hydrolysis did not occur. Addition of water vapor to the adsorbed species caused a slow hydrolysis, marked by the disappearance of the 1225 cm^{-1} band and the appearance of absorptions at 1134 and 1070 cm^{-1}. Hence it follows that the hydrolysis of adsorbed DMPF is retarded by HF.

These two experiments show that an acid, i.e., HF, retards the conversion from structure **I** to **II**. This might imply that a base will accelerate the reaction. For experimental reasons we have preferred to study the hydrolysis of sarin on magnesia to that on, e.g., a sodium-doped alumina. Magnesia is known to behave as a basic catalyst (*7, 23, 24*). An advantage of using

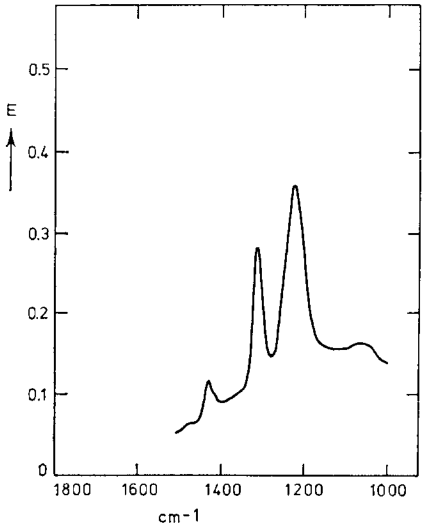


FIG. 8. DMPF/Al_2O_3–HF.

magnesia is the transparency of the material in the 1000–800 cm^{-1} frequency range.

C. When sarin was adsorbed on magnesia the spectrum shown in Fig. 9 was observed. Most adsorbed sarin molecules have structure **II** [absorption at 1170 and 1070 cm^{-1}]. Some structure **I** may be observed {the weak band at 1255 cm^{-1} (P=O), the shoulder at 1020 cm^{-1} [C–O–(P)] and the small band at 840 cm^{-1} (P–F!)}. These three absorptions have disappeared after 100 min (or after addition of water). This experiment proves that (a) relative to alumina, the hydrolysis of adsorbed sarin proceeds considerably faster on magnesia, and (b) that structure **I** contains a P–F bond, which is absent in structure **II**.

D. Experiment C has been repeated with DMPF instead of sarin (Fig. 10). The strong bands at 1160 and 1080 cm^{-1} must be attributed to POO stretchings. The shoulders at about 1230 and 810 cm^{-1} point to some structure **I**.

Two more experiments have been performed, with sarin and DMPF, respectively, on magnesia that had been pretreated with HF. In both cases little material was adsorbed; possibly adsorption was mainly physical or weakly chemical. Anyhow, no evidence for the occurrence of structure **II** could be observed.

The conclusion that may be drawn from these experiments is that the conversion of structure **I** into **II** (i.e., the hydrolysis of adsorbed sarin) is a base initiated reaction; the active sites are poisoned by hydrogen fluoride.

Another series of experiments has been performed to determine the influence of the quantity of adsorbed water on the activity of the alumina with respect to the surface reaction under investigation. The results demonstrated that surface hydroxyl groups and adsorbed water do not play an important part in the adsorption of sarin on alumina. Sarin adsorbs on wet alumina as well as on alumina pretreated at 900°C *in vacuo*. Apparently sarin molecules remove hydroxyl groups from adsorption centers; these displaced hydroxyls are met again at the surface as hydrogen bonded or water-like structures, absorbing radiation of 3600–3000 cm^{-1}. On the other hand, infrared spectra of sarin adsorbed on alumina pretreated at 900°C revealed that hydrolysis did not occur. Consequently, adsorbed water and/or hydroxyl groups are involved in the hydrolysis of sarin on γ-alumina. When sarin was adsorbed on "wet" alumina (water vapor added prior to sarin) structure **II** proved to have developed in excess of structure **I**.

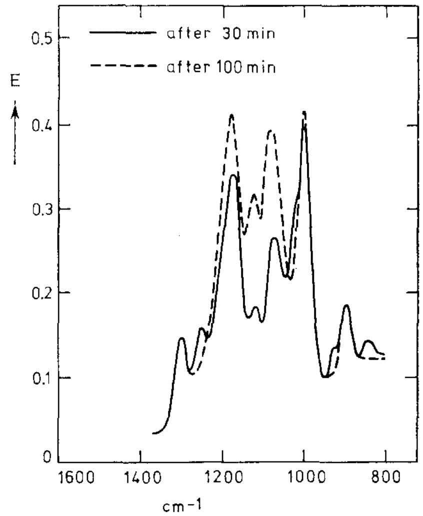


FIG. 9. Sarin/MgO.

In view of these results and knowing the influence which HF has on the hydrolysis of sarin it is interesting to see what kind of alterations in the O–H stretching region of the spectrum are produced by adsorption of HF on alumina.

With an evacuated alumina disk in the reference cell the spectrum of Fig. 11 was recorded after HF adsorption and evacuation. A negative band at 3720 cm^{-1} indicates the disappearance of OH groups from the sample disk. The broad absorption around 3400 cm^{-1} is again observed; however, an absorption at 3600 cm^{-1} occurs, not observed earlier. Figure 4 shows that in the spectrum of adsorbed HF a strong band at 1120 cm^{-1} appears, which

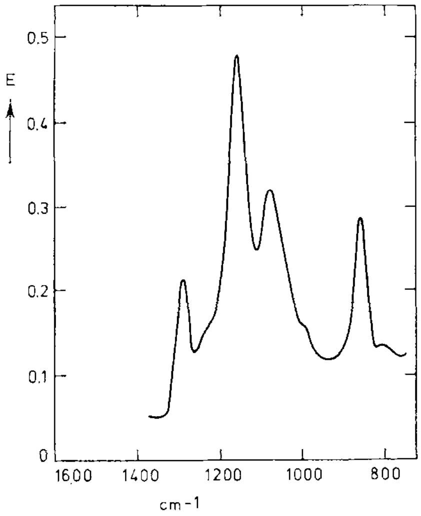


FIG. 10. DMPF/MgO.

probably results from an Al–F stretching (*25*). Hence the adsorption of HF can be described by the reaction

$$\mathrm{HF} + \underset{(3720\ \mathrm{cm}^{-1})}{\mathrm{Al\text{-}OH}} \rightarrow \underset{(1120\ \mathrm{cm}^{-1})}{\mathrm{Al\text{-}F}} + \underset{\substack{(3400\ \mathrm{cm}^{-1})\\(1660\ \mathrm{cm}^{-1})}}{\mathrm{HOH}}.$$

From the effect of fluoride on γ-alumina Peri (*25*) has concluded that the properties of sites adjacent to fluorided centers are inductively modified. The absorption at 3600 cm^{-1} may possibly originate from these "acidified" hydroxyls.

Figure 7 demonstrates that the adsorption of sarin on HF pretreated alumina is not measurably hindered, as was confirmed by quantitative measurements (*6*). The 1120 cm^{-1} absorption is not seriously affected upon sarin adsorption either. Evidently just a fraction of the surface hydroxyls is exchanged by the fluoride. Nevertheless, hydrolysis of the adsorbed organophosphorus compound is drastically reduced. This effect cannot be explained only by the disappearance of surface hydroxyls as a consequence of exchange but must originate to a substantial extent from the poisoning influence of the fluoride on its neighboring hydroxyl groups.

Dealkylation of Adsorbed Sarin

With alumina or magnesia disks in the infrared beams of the spectrometer the experimental circumstances are far from ideal to observe any desorbed reaction product. For this reason an experiment was performed with a large quantity of Ketjen alumina (16 g), situated out of the path of the infrared beam in the sample cell. The reference cell was not charged. After evacuation of the cells sarin was admitted to the alumina for adsorption. The cell was then closed. The adsorption was very fast as no sarin bands could be detected shortly after dosing. After 15 hr a spectrum of the vapor phase, due to desorption, was recorded. This spectrum concurred with that of propene and showed also a small $\mathrm{CO_2}$ band at 2340 cm^{-1}. By raising the temperature of the cell all absorption bands gained intensity, but no new band appeared.

The formation of propene proves that another decomposition reaction of adsorbed sarin is proceeding, one in which the iso-

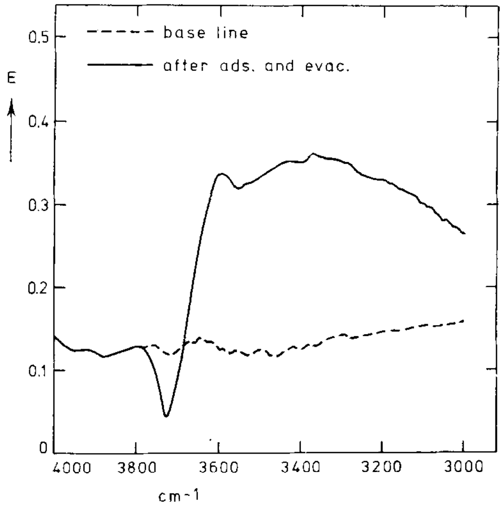
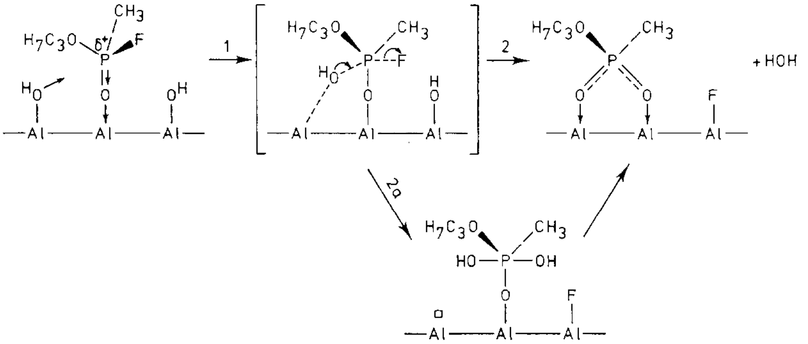


FIG. 11. Effect of HF adsorption on the surface hydroxyls of alumina.

propyl group is released. Since a volatile reaction product is liberated with this dealkylation the reaction can be followed easily and accurately by means of a gas-chromatographic technique (*6*). From the amount of propene detected it followed that the dealkylation proceeds extremely slowly: just about 2% of the adsorbed sarin molecules had dealkylated after 1 week. By modifying the adsorbent it could be established that the dealkylation is activated by strongly acid sites: high temperature pretreatment of the alumina or pre-adsorbed HF appeared to increase the rate of propene formation considerably, whereas the reaction could be completely poisoned by addition of water.

DISCUSSION

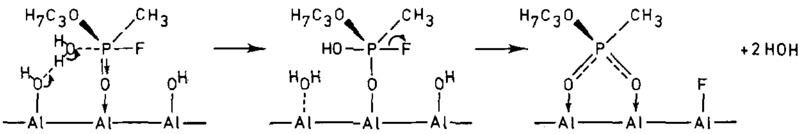
It has been shown that the hydrolysis of adsorbed sarin is activated by basic surface sites. The experiments with adsorbents pretreated with HF or at high temperatures prove that surface hydroxyls are involved. The conversion of structure **I** into **II** may therefore be represented by a substitution of the fluorine by a hydroxyl group. As in alkaline hydrolysis of organophosphorus compounds, such a displacement reaction is likely to proceed via a transition state with a five-coordinate phosphorus [see e.g., Ref. (*26*)]. The most probable reaction path may be represented schematically:



SCHEME A

Step 1 is assumed to be rate determining, because of the kinetics of the reaction [discussed in the following papers (*29*)]. The situation in the transition state is more or less similar to that in alkaline hydrolysis; the fluorine is ejected, leaving an acidic phosphonium ion. This compound may now either lose its proton and form structure **II** (step 2) or participate in another nucleophilic displacement (step 2a), resulting in the same product. Water produced with this reaction is adsorbed on the surface; it may compete with the poisoning effect of the adsorbed fluorine as it has appeared to accelerate the hydrolysis considerably.

This effect of water may be ascribed to the formation of new surface hydroxyls, thus increasing the number of active sites. This will undoubtedly play a part on aluminas pretreated *in vacuo* at higher temperatures. Alumina pretreated at room temperature is completely covered with water and the influence of extraneous water cannot be understood in that case. Therefore, it seems more appropriate to consider the introduction of a water molecule as a fifth ligand to phosphorus (*26*, *27*). The promoting effect of water on the rate of reaction is then explained by the acceleration of the first and rate-determining step. Considering the kinetics of the reaction with water (*6*), indicating that the reaction is still controlled by the surface, the following mechanism seems plausible:



SCHEME B

The more basic the hydroxyl with which the water ligand is associated, the more nucleophilic (= reactive) this water molecule will be. The mechanism proposed in Scheme B explains why addition of water to sarin adsorbed on HF-pretreated alumina, does not induce any hydrolysis: there are no basic hydroxyls to initiate the reaction.

The proposed adsorption structures as well as their interactions with the surface must be conceivable in terms of the lattice structure of the preferentially exposed alumina plane. According to Lippens (*28*) it is very probable that the (110) plane of spinel is exposed in the case of γ-alumina. In the spinel lattice parallel to the (110) plane, two types of cation distributions are present, referred to as the C- and D-layers, which are stacked on each other as CDCDC, etc. When exposed at the surface these layers are no longer completely compensated for their electric charge by each other. Compensation is attained by adsorption of hydroxyl groups on aluminum ions (C-layer) or by protons joining oxygens (D-layer).

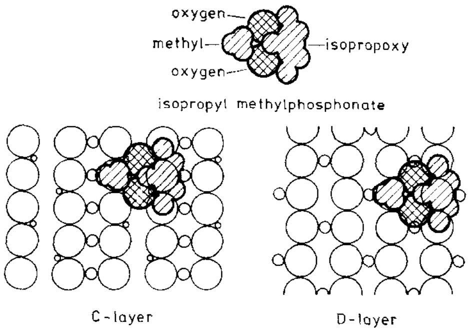


FIG. 12. Proposed orientation of hydrolyzed adsorbed sarin on the (110) plane of γ-alumina.

When structure **II** has been formed two neighboring aluminum ions are involved in the adsorption complex. This situation is indicated in Fig. 12. It appears that the spacing of the oxygen atoms of the POO grouping is in perfect harmony with the oxygen positions in the (110) plane.

Figure 12 allows us to calculate the amount of sarin that can be adsorbed in a monolayer. An adsorbed sarin molecule occupies a rectangular area of the oxygen lattice of 7.47 × 5.28 = 39.43 Å^2 (the radius of the oxygen ion is taken 1.32 Å). Hence it follows that 1 mg adsorbed sarin covers 1.69 m^2 of the (110) plane of γ-alumina. Adsorption experiments revealed that the quantity of sarin adsorbed on Ketjen alumina which cannot be removed by prolonged evacuation at room temperature amounts to 165 mg/g adsorbent. From a surface area of 280 m^2/g for this alumina it follows that 1 mg of chemisorbed sarin covers 1.70 m^2 of the alumina surface, which is in excellent agreement with the value calculated from Fig. 12.

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