

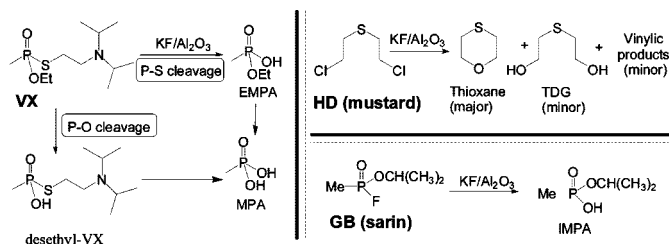
Facile Hydrolysis-Based Chemical Destruction of the Warfare Agents VX, GB, and HD by Alumina-Supported Fluoride Reagents

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A facile solvent-free hydrolysis (chemical destruction) of the warfare agents VX (*O*-ethyl *S*-2-(diisopropylamino)ethyl methylphosphonothioate), GB (*O*-isopropyl methylphosphonofluoridate or sarin), and HD (2,2'-dichloroethyl sulfide or sulfur mustard) upon reaction with various solid-supported fluoride reagents is described. These solid reagents include different alumina-based powders such as KF/Al₂O₃, AgF/KF/Al₂O₃, and KF/Al₂O₃ enriched by so-called coordinatively unsaturated fluoride ions (termed by us as ECUF-KF/Al₂O₃). When adsorbed on these sorbents, the nerve agent VX quickly hydrolyzed (*t*_{1/2} range between 0.1–6.3 h) to the corresponding nontoxic phosphonic acid EMPA as a major product (>90%) and to the relatively toxic desethyl-VX (<10%). The latter byproduct was further hydrolyzed to the nontoxic MPA product (*t*_{1/2} range between 2.2–161 h). The reaction rates and the product distribution were found to be strongly dependent on the nature of the fluoride ions in the KF/Al₂O₃ matrix and on its water content. All variations of the alumina-supported fluoride reagents studied caused an immediate hydrolysis of the highly toxic GB (*t*_{1/2} < 10 min) to form the corresponding nontoxic phosphonic acid IMPA. A preliminary study of the detoxification of HD on these catalyst supports showed the formation of the nontoxic 1,4-thioxane as a major product together with minor amounts of TDG and vinylic compounds within a few days. The mechanisms and the efficiency of these processes were successfully studied by solid-state ³¹P, ¹³C, and ¹⁹F MAS NMR.

Introduction

Detoxification of extremely toxic chemical warfare agents (CWA) such as VX, GB (sarin), and HD (sulfur mustard) is a current concern. Rapid removal of CWA from diverse surfaces is required in order to regain use of the affected area and equipment. Reactive decontaminants that chemically destroy CWA rather than simple physical removal, as in the case of the Fuller's earth sorbent, are favored.^{1–5} They should be characterized by a capability to neutralize CWA in a rapid and safe manner, ease of handling, stability in long-term storage,

availability, and easy disposal. Inorganic oxide powders may comply with these requirements due to their unique surfaces that possess a large number of basic and acidic Brönsted and Lewis sites, which can significantly accelerate hydrolysis processes. They are also environmentally benign and benefit from lack of corrosiveness and low cost. Following these requirements, Wagner et al. have reported on the reactions of neat liquid VX, GD (soman), and HD with the nanosize inorganic oxide particles MgO,¹ CaO,² NaY, and AgY zeolites³ and alumina.⁴ Although these three CWAs were found to undergo a room-temperature hydrolysis (chemical destruction) on the surface of the above-mentioned inorganic oxides, the reactions were limited by their diffusion capability, which reduced the overall reaction rates (a *t*_{1/2} range between hours to days). In addition, these metal oxides nanoparticles were found to be unstable in the presence of air or moisture. Overcoming

[†] These authors contributed equally.

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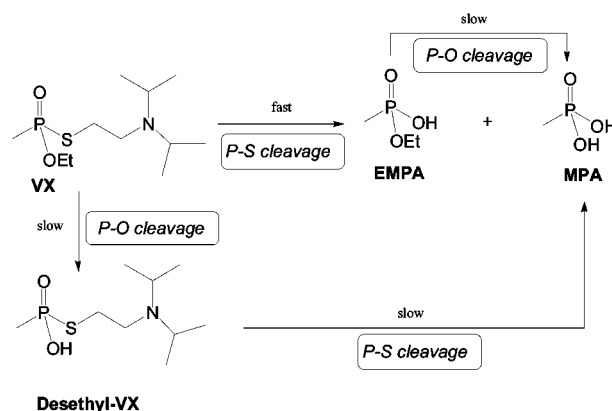
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these drawbacks, the same author has recently reported that VX, GD, and HD rapidly hydrolyzed ($t_{1/2}$ between minutes to hours) under the action of nanotubular titania.⁵ Spafford reported on immediate decomposition of VX by using powder AgF,⁶ however, formation of the toxic “G-analogue” byproduct is a significant disadvantage of this method.

Supporting reagents on inorganic oxides, such as alumina, silica, zeolites, and clays, is a well-known approach to increase reactivity or selectivity of these solid supports catalysts. For example, adsorption of potassium fluoride on the surface of neutral alumina (KF/Al₂O₃) results in the formation of a basic heterogeneous catalyst. This catalyst was found to be a convenient and efficient solid support for a variety of substitution, elimination, addition, and condensation reactions.^{7,8} However, the source of its basicity and the identity of its catalytic sites are still ambiguous. It is well-known that a thermal reaction of KF with Al₂O₃ in the presence of water can give K₃AlF₆ as a product together with KOH (eq 1). Weinstock et al. have shown that in the base-catalyzed reaction of chloroform with *m*-nitrobenzaldehyde no differences in the reaction yield/kinetic were observed when KF/Al₂O₃ versus KOH/Al₂O₃ were used as basic solid supports.⁹ Therefore, they claimed that the basicity of KF/Al₂O₃ arises only from the KOH base formed in the initial preparation of the solid support. On the other hand, Ando¹⁰ and Clark¹¹ and their co-workers demonstrated that additional to the formation of KOH on the surface of KF/Al₂O₃, the remaining coordinatively unsaturated fluoride ions (i.e., not bound to Al³⁺ ions)¹² might play a crucial role in activity of this solid support. Intensification to this argument was obtained by a series of experiments performed by the same authors¹³ and others¹⁴ using

SCHEME 1



analytical methods such as titration, IR, solid-state ¹⁹F MAS NMR and XRD.



In this paper we wish to present our results on the effects of alumina-based fluoride reagents (MF/Al₂O₃ powders) as convenient and efficient reactive sorbents for rapid hydrolysis and detoxification of the CWAs VX, GB, and HD. The solid-state ³¹P, ¹⁹F, and ¹³C MAS NMR was applied as a detection technique, which allowed sample study in real time and in a nondestructive manner.^{1–5,15,16}

Results and Discussion

Destructive Adsorption of VX on KF/Al₂O₃. Scheme 1 represents two possible routes in the basic hydrolysis of VX. This study is focused both on the P–S cleavage route (fast and favored process), leading to the nontoxic EMPA product, and on the P–O cleavage route that leads to the relatively toxic desethyl-VX byproduct (slow and not favored process). In our study, all the reactions of VX with KF/Al₂O₃ led to EMPA as a major product and in some cases together with the undesired desethyl-VX byproduct (as previously observed in reactions performed in basic aqueous solution). Nevertheless, this minor byproduct was further degraded by a second slow hydrolysis to the final nontoxic MPA product. Obviously, in basic conditions both EMPA and MPA products are eventually deprotonated to their corresponding phosphonate salts.

In the course of this study, several types of alumina powders (i.e., neutral γ -Al₂O₃, basic Al₂O₃, and KF/Al₂O₃) were initially tested as simple reactive sorbents for chemical destruction of VX, by means of a heterogeneous basic hydrolysis. The various KF/Al₂O₃ supports were found to be chemically different as a function of their preparation conditions. Therefore, the identification of each KF/Al₂O₃ support will be expressed by its KF loading percent, preparation medium, and drying temperature, respectively, summarized in the attached parenthesis. For example, the expression KF/Al₂O₃ (20, H₂O, 160) refers to KF/Al₂O₃ that contains 20wt % of KF, prepared in water, and finally dried at the temperature of 160 °C.

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TABLE 1. Hydrolysis Rates of VX Adsorbed on Alumina-Based Powders

run	solid used	VX (wt %)	H ₂ O (wt %)	<i>t</i> _{1/2} (h) ^a	EMPA (%)	desethyl-VX	
						%	<i>t</i> _{1/2} (h) ^b
1	KF/Al ₂ O ₃ (40, H ₂ O, 160)	5	0	~1200	50		
2	KF/Al ₂ O ₃ (40, H ₂ O, 160)	5	5	6.3	91	9	161
3	KF/Al ₂ O ₃ (40, H ₂ O, 160)	5	10	11.2	91	9	nd ^c
4	KF/Al ₂ O ₃ (20, H ₂ O, 160)	5	5	3.0	93	7	nd ^c
5	KF/Al ₂ O ₃ (20, H ₂ O, 160)	5	10	2.9	93	7	50
6	KF/Al ₂ O ₃ (10, H ₂ O, 160)	5	5	6.1	88	12	330
7	KF/Al ₂ O ₃ (20, H ₂ O, 160)	10	5	2.6	93	7	nd ^c
8	KF/Al ₂ O ₃ (20, H ₂ O, 160)	25	5	nd ^c	84	5	nd ^c
9	neutral alumina	5	5	11.2	100		
10	basic alumina	5	5	6.6	100		
11	KOH/Al ₂ O ₃ (20, H ₂ O, 160)	5	5	5.6	85	15	nd ^c

^a Half-life of pseudo-first-order reaction. ^b Half-life of the hydrolysis of desethyl-VX to MPA. ^c Half-life time was not determined.

The real-time kinetic results of the hydrolysis process were extracted from the solid-state ³¹P MAS NMR spectra and are summarized in Table 1. In a typical experiment 2 μL of VX was carefully added, without mixing or crushing, to the examined powder (ca. 40 mg, wetted with 5% water) placed in the NMR rotor. Monitoring the reaction by ³¹P MAS NMR spectroscopy revealed that the signals assigned for VX and desethyl-VX side product (at 55 and 38 ppm, respectively) were fairly narrow and well separated from the relatively broader signals assigned for the nontoxic products EMPA and MPA (at ca. 25 and 20 ppm, respectively). Thus, the integration of the NMR signals of both the starting material and the products should be proportional to the concentration of the adsorbed compounds and therefore can be monitored for determining the rate constants of the reactions. The broadness of the solid-state MAS NMR signals is determined by the nature of the tested adsorbed compound. Namely, cases in which the adsorption is physical (compounds are mobile on the surface), rather than chemical, will lead to relatively narrow peaks, and vice versa. It will be shown that in the present study, this feature was strongly affected by the reaction conditions.

Inspection of the data presented in Table 1 revealed that KF/Al₂O₃ supports can easily hydrolyze VX, at different rates and at ambient temperature. A typical picture of ³¹P MAS NMR spectra for the monitoring of VX hydrolysis onto KF/Al₂O₃ (40, H₂O, 160) and its reaction profile are depicted in Figure 1. Both in terms of the reaction kinetics and the nature of the products, the reactions were dependent on three parameters: the water content of the powder (Table 1, runs 1–5), the percentage loading of KF on the alumina (runs 2, 4, and 6), and the concentration of VX in the sorbent (runs 4, 7 and 8). It was found that the rate of the hydrolysis reaction was slowed by either a lack (0–2%) or an excess (10%) of water added to the KF/Al₂O₃ (40, H₂O, 160) or KF/Al₂O₃ (20, H₂O, 160) powders prior to the addition of VX (runs 1–5). It is reasonable to assume that excess of water molecules may block the active sites of the solid catalyst or enhance its hydrophilicity, in such a way that the diffusion of VX is slowed down. On the other hand, in the absence of water molecules the hydrolysis process is very slow, despite the amount of hydroxide ions available in the KF/Al₂O₃ (40, H₂O, 160) support (run 1). This observation implies that the hydrolysis occurred by the assisting of water additive in a cooperative mechanism (vide infra). Thus, the addition of water (5%) as a reactant, which did not affect the flowing nature of the powder, is necessary for obtaining optimal reproducible results at ambient temperature.

The reaction studies indicate that 20% KF loading (compared to 10% and 40%) results in a more effective hydrolysis reagent,

expressed by a more rapid rate reaction and lower percentage of the desethyl-VX byproduct (runs 2, 4, and 6; Figures 1 and S3 and S5, Supporting Information). It is known that the original surface area of the alumina starting material is not considerably affected by the preparation procedure in cases in which a low loading of KF (<5 mmol/g) or a low drying temperature (<200 °C) are used.^{11,13,14} It seems that higher loading of KF (40%, 8.4 mmol/g) causes a decrease in the surface area of the alumina support,¹¹ while lower loading of this salt (10%) results in a matrix with less amount of active sites. In addition, we found that the rate of the hydrolysis was not affected by the concentration of VX, using KF/Al₂O₃ (20, H₂O, 160) with 5% water at ambient temperature (runs 4 and 7; Figures S3 and S6, Supporting Information). At these conditions, the concentration limit for VX full hydrolysis was found to be somewhere between 20% and 25%, a very high concentration for any possible scenario.

In most cases, the profiles of the hydrolysis of both VX and desethyl-VX were found to be compatible with a pseudo-first-order reaction, suggesting that the diffusion of the reactant toward the active sites is the rate-determining step (Figures 1 and S2–S6, Supporting Information).

Interestingly, subjection of VX to a commercial neutral or basic Al₂O₃, using water as an additive (5 wt %) resulted in the formation of the nontoxic EMPA product in a quantitative yield, without formation of desethyl-VX byproduct (runs 9 and 10). Moreover, the hydrolysis rate under the action of basic Al₂O₃ was fairly close to that of the more basic KF/Al₂O₃ (40, H₂O, 160) at the same conditions (runs 2 and 10). In addition, from a kinetic point of view, the performance of wetted neutral Al₂O₃ (5 wt %) in its ability to hydrolyze VX at ambient temperature is impressive by itself. It seems that the difference between our experiments with neutral Al₂O₃ and the reactions of VX with nanosize Al₂O₃, reported by Wagner et al.,⁴ stems from the presence or the absence of water as an additive. This feature may affect the mechanism of the hydrolysis and therefore the rate of the reaction and the nature of the products (vide infra).

One way to estimate the effectiveness of KF/Al₂O₃ as a heterogeneous basic catalyst for organic transformations is to compare it with KOH/Al₂O₃ support, considering both the selectivity and the kinetics of the reaction. Thus, comparing the hydrolysis of VX onto KF/Al₂O₃ (20, H₂O, 160) vs KOH/Al₂O₃ (20, H₂O, 160) revealed that the former support is more effective not only by terms of reaction rate (ca. 2-fold higher) but also in terms of products distribution (runs 4 and 11). Taking into account that the reaction of KF with Al₂O₃ may produce a 0.5 equiv of KOH depending on the preparation conditions,⁷ KOH/Al₂O₃ (20, H₂O, 160) contains more hydroxide ions per

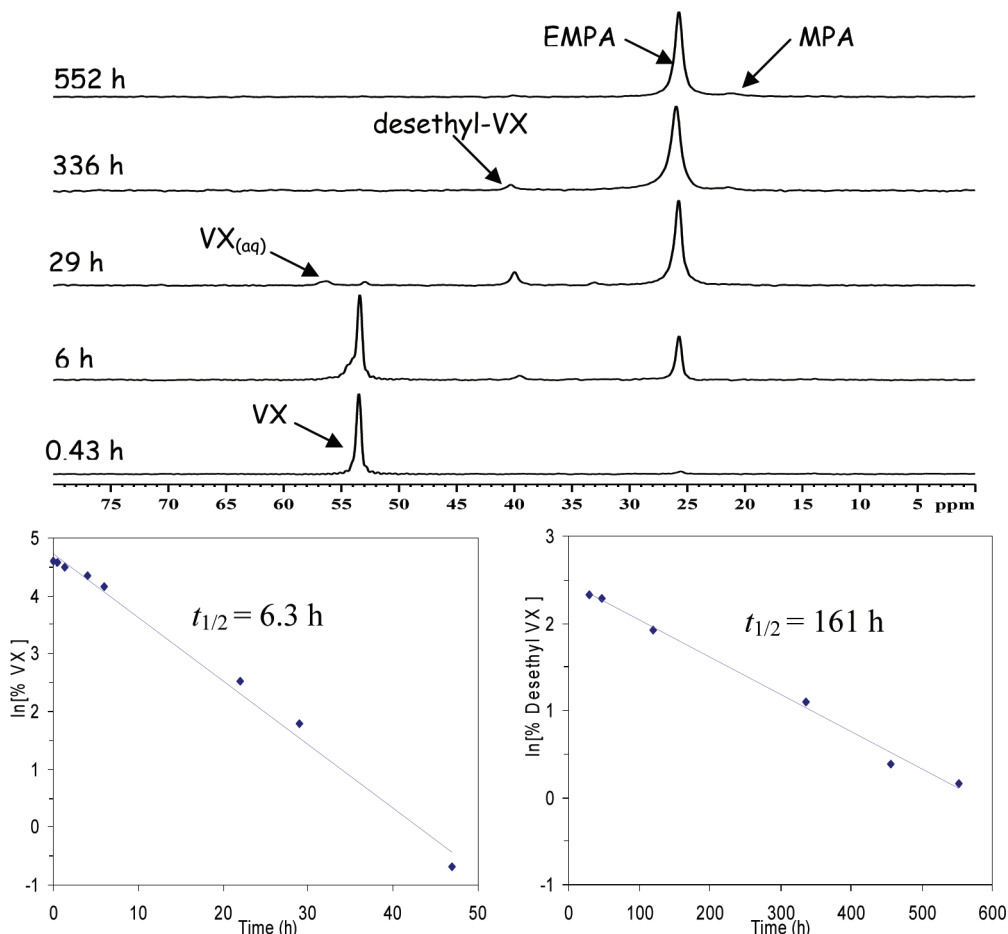


FIGURE 1. Selected ^{31}P MAS NMR spectra of adsorbed VX (5 wt %) on $\text{KF}/\text{Al}_2\text{O}_3$ (40, H_2O , 160) using H_2O (5%) as an additive (top) and degradation profiles of VX (bottom left) and desethyl-VX (bottom right) onto this sorbent.

weight than that of $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 160) according to eq 1. Therefore, comparing the hydrolysis of VX onto $\text{KF}/\text{Al}_2\text{O}_3$ (40, H_2O , 160) versus $\text{KOH}/\text{Al}_2\text{O}_3$ (20, H_2O , 160) is more indicative regarding the role of other species than hydroxide ions (such as coordinately unsaturated fluoride ions), in determining both kinetics and products of the reaction. Inspection of the data presented in Table 1 (runs 2 and 11) reveals that the reaction rates on these two solid supports are fairly close, but the product distribution is somewhat different (9% vs 15% of the side product desethyl-VX, respectively). This observation clearly shows that in terms of the reaction kinetics, there is no difference between these two solid supports, and therefore, it seems that the involvement of “free” fluoride ions in the acceleration of VX hydrolysis onto $\text{KF}/\text{Al}_2\text{O}_3$ (40, H_2O , 160) is particularly minor.

From the above-mentioned results one may deduce that standard $\text{KF}/\text{Al}_2\text{O}_3$ compared to $\text{KOH}/\text{Al}_2\text{O}_3$ or even commercial basic alumina as solid supports for VX hydrolysis showed no significant advantages. Therefore, we decided to further investigate the performance of this inorganic catalyst by modification of its preparation conditions.

$\text{KF}/\text{Al}_2\text{O}_3$ Enriched with Coordinately Unsaturated F^- ions (ECUF- $\text{KF}/\text{Al}_2\text{O}_3$). Interestingly, the hydrolysis of VX onto $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 100), dried at 100°C instead of 160°C , was found to be 4-fold faster than that performed onto its $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 160) counterpart (Table 2, runs 1 and 2). These two solid supports were compared in their solid-state ^{19}F -MAS NMR spectroscopy. The spectrum of $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O ,

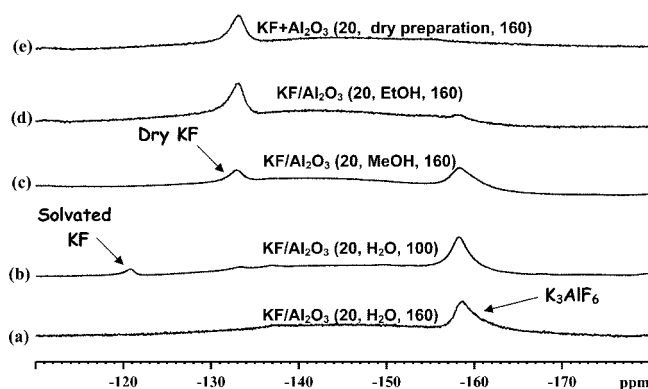
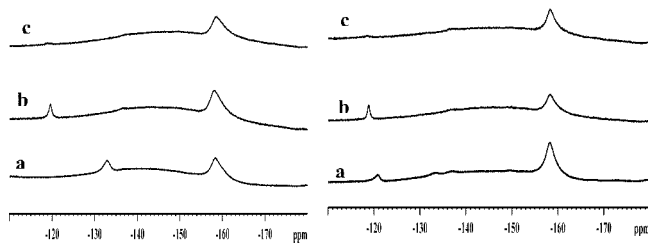
160) gave a single peak at -158 ppm that is attributed to K_3AlF_6 (Figure 2a),^{13,14} whereas in the spectrum of $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 100), an additional peak appeared at -121 ppm (Figure 2b). The assignment for this signal is KF solvated by water (drying at 100°C leaves out sufficient amounts of water molecules for this solvation), which means that not all of the fluorine atoms are bound to the aluminum atoms.¹³ Moreover, when the hydrolysis of VX with $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 100) was monitored by both ^{31}P and ^{19}F -MAS NMR spectroscopy, this signal disappeared in parallel to the reaction progression (Figure 3, right). Obviously, this is direct evidence for the participation of the coordinately unsaturated fluoride ions in an organic reaction, catalyzed by $\text{KF}/\text{Al}_2\text{O}_3$. In view of the fact that $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 160) and $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 100) are different not only by their performance to accelerate VX hydrolysis but also by their chemical composition, we chose to term the latter catalyst as ECUF- $\text{KF}/\text{Al}_2\text{O}_3$, which means $\text{KF}/\text{Al}_2\text{O}_3$ enriched with coordinately unsaturated F^- ions.

In view of this result, we attempted a different preparation approach in which dry alumina and dry KF are ground together without the involvement of water. This may prevent the formation of K_3AlF_6 and enrich the KF component in the solid support. Indeed, this $\text{KF}/\text{Al}_2\text{O}_3$ (20, dry, 160) gave only the characteristic peak for dry KF at -132 ppm (Figure 2e).¹³ However, this solid support did not exhibit significant advantage in the hydrolysis of VX, compared to the standard $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 160), except for the fact that the process was completed with no formation of desethyl-VX (Table 2, runs 1

TABLE 2. Hydrolysis Rates of VX Adsorbed on ECUF-KF/Al₂O₃ Powders

run	KF/Al ₂ O ₃ used	added H ₂ O (%)	<i>t</i> _{1/2} (h) ^a	EMPA (%)	desethyl VX	
					%	<i>t</i> _{1/2} (h) ^b
1	KF/Al ₂ O ₃ (20, H ₂ O, 160)	5	2.7	93	7	nd ^c
2	KF/Al ₂ O ₃ (20, H ₂ O, 100)	5	0.7	93	7	nd ^c
3	KF/Al ₂ O ₃ (40, H ₂ O, 160)	5	6.3	91	9	161
4	KF/Al ₂ O ₃ (40, MeOH, 160)	0	21 ^d	100		
5	KF/Al ₂ O ₃ (40, MeOH, 160)	2	2.2 ^d	100		
6	KF/Al ₂ O ₃ (40, MeOH, 160)	5	0.26	96	4	2.2
7	KF/Al ₂ O ₃ (40, MeOH, 160)	10	0.5	94	6	5.6
8	KF/Al ₂ O ₃ (20, MeOH, 160)	5	0.26	96	4	2.6
9	KF/Al ₂ O ₃ (20, EtOH, 160)	5	0.22	100		
10	KF/Al ₂ O ₃ (20, dry, 160)	5	4.6	96		

^a Half-life of pseudo-first-order reaction. ^b Half-life of the hydrolysis of desethyl VX to MPA. ^c Half-life time was not determined. ^d This is the first and short *t*_{1/2} originating from two half-life times observed by the reaction profile of these reactions (see Figures S8 and S9, Supporting Information).

FIGURE 2. ¹⁹F MAS NMR spectra of several KF/Al₂O₃ sorbents.FIGURE 3. ¹⁹F MAS NMR spectra of KF/Al₂O₃ (20, H₂O, 100) (right) and KF/Al₂O₃ (20, MeOH, 160) (left): (a) the dry sorbent, (b) after addition of 5% water, and (c) after the reaction with VX.

and 10). We assume that despite the stringent grinding of the two dry solids, the dispersion of free fluoride ions in the pores of the alumina matrix is limited intrinsically by the size of KF particles. In order to enhance the dispersity of KF in the KF/Al₂O₃ support along with the prevention of K₃AlF₆ formation, the latter was prepared in dry methanol instead of water and then dried at 160 °C. The remaining KF peak at -132 ppm implied that again this modification in KF/Al₂O₃ preparation left out a significant amount of free fluoride ions dispersed in the sorbent (Figure 2c). These catalysts, i.e., KF/Al₂O₃ (40, MeOH, 160) and KF/Al₂O₃ (20, MeOH, 160), were found to be much more reactive both in the hydrolysis of VX and desethyl-VX (Figure 4), than their “aqueous preparation” counterparts (runs 1, 3 vs 8, 6, respectively). The addition of 5% water as additive is recommended in order to accomplish the hydrolysis process in a fast manner (Table 2, runs 4–7; see also Figures S7–S9, Supporting Information). The same reactivity of the higher loading KF/Al₂O₃ (40, MeOH, 160) compared to its lower loading counterpart KF/Al₂O₃ (20, MeOH, 160) revealed that this preparation method did not affect the surface area of the support by high KF impregnation. Again,

direct evidence to the participation of coordinatively unsaturated fluoride ions in the hydrolysis process was achieved by monitoring the reaction with both ³¹P and ¹⁹F MAS NMR (Figure 3, left). Interestingly, in these reactions the compound *O*-ethyl-*O*-methyl methylphosphonate (EMMP) was also observed as a minor byproduct resulting from traces of methoxide ions present in this solid support (see Figures 4 and S7, Supporting Information).

Similarly, preparation of KF/Al₂O₃ (20, EtOH, 160), in which ethanol was used as a solvent, left almost all free fluoride ions in the sorbent, and only a small quantity of K₃AlF₆ was formed (Figure 2d). The hydrolysis of VX onto this support was found to be faster than that of KF/Al₂O₃ (20, MeOH, 160), supposedly due to the present of large amounts of coordinatively unsaturated fluoride ions (Table 2, run 9).

Effect of Silver Ion by AgF Impregnation. These results encouraged us to further improve the activity of the powder by investigating the effect of silver ion impregnated on the alumina-based fluoride reagent on the hydrolysis of VX. The rationale of this approach is based on previous results reported by Wagner et al.,³ who demonstrated that AgY zeolites can chemically destruct VX agent, by the well-known activation of the P–S bond.¹⁷ Indeed, impregnation of AgF instead of KF in neutral alumina resulted in the formation of an improved solid support to the VX hydrolysis purpose. Thus, when using AgF/Al₂O₃ (40, H₂O, 160), the hydrolysis of VX at the same conditions was 3.9-fold faster compared to KF/Al₂O₃ (40, H₂O, 160) as solid support (Table 3, runs 1–2). Moreover, a composition of AgF (5 wt %), KF (35 wt %), and neutral alumina gave a very effective solid support, in which the hydrolysis of VX occurred more than 60-fold faster (with *t*_{1/2} < 0.1 h) when compared to the usual KF/Al₂O₃ (Figure 5; Table 3, run 4). Expectedly, the hydrolysis of desethyl-VX was also enhanced using this solid support (Figure 5, right; see also Figures S10 and S11, Supporting Information). In dry conditions, the AgF/KF/Al₂O₃ (5, 35, H₂O, 160) powder also chemically destroyed VX, in a relatively fast manner (Table 3, run 6).

The reaction profiles for the VX hydrolysis onto selected KF/Al₂O₃ sorbents depicted in Figure 6 clearly show the influence of these procedural modifications on the reaction kinetics. The impressive performance of AgF/KF/Al₂O₃ and ECUF-KF/Al₂O₃ in the hydrolysis-based chemical destruction of both VX and desethyl-VX strongly emphasizes their potential utilization as a destructive powder for the decontamination of CWA. To the best of our knowledge, the hydrolysis process onto wetted (5%)

(17) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; pp 942–943.

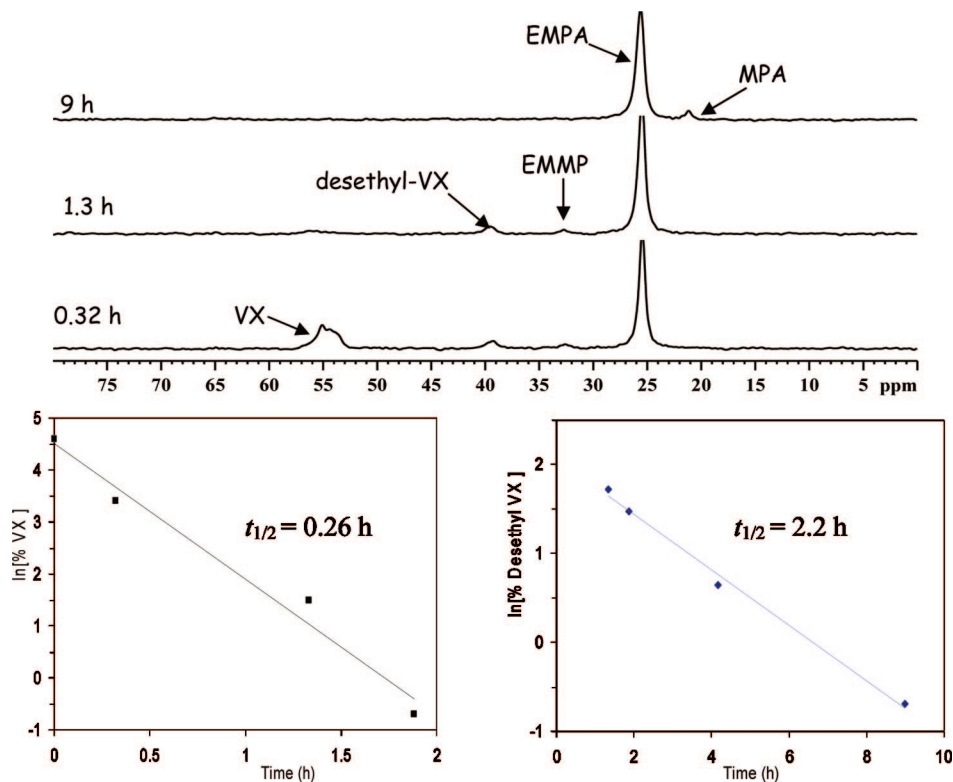


FIGURE 4. Selected ³¹P MAS NMR spectra of adsorbed VX (5 wt %) on KF/Al₂O₃ (40, MeOH, 160) using H₂O (5%) as an additive (top) and degradation profiles of VX (bottom left) and desethyl-VX (bottom right) onto this sorbent.

TABLE 3. Hydrolysis Rates of VX Adsorbed on Alumina-Supported AgF Powders

run	solid used	H ₂ O (wt %)	$t_{1/2}$ (h) ^a	EMPA (%)	desethyl-VX	
					(%)	$t_{1/2}$ (h) ^b
1	KF/Al ₂ O ₃ (40, H ₂ O, 160)	5	6.3	91	9	161
2	AgF/Al ₂ O ₃ (40, H ₂ O, 160)	5	1.6	99	1	
3	AgF/KF/Al ₂ O ₃ (5, 35, H ₂ O, 160)	10	0.28	90	10	2.8
4	AgF/KF/Al ₂ O ₃ (5, 35, H ₂ O, 160)	5	<0.1	90	10	1.8
5	AgF/KF/Al ₂ O ₃ (5, 35, H ₂ O, 160)	2	0.53	96	4	4.8
6	AgF/KF/Al ₂ O ₃ (5, 35, H ₂ O, 160)	0	22.4	99		

^a Half-life of pseudo-first-order reaction. ^b Half-life of the hydrolysis of desethyl-VX to MPA.

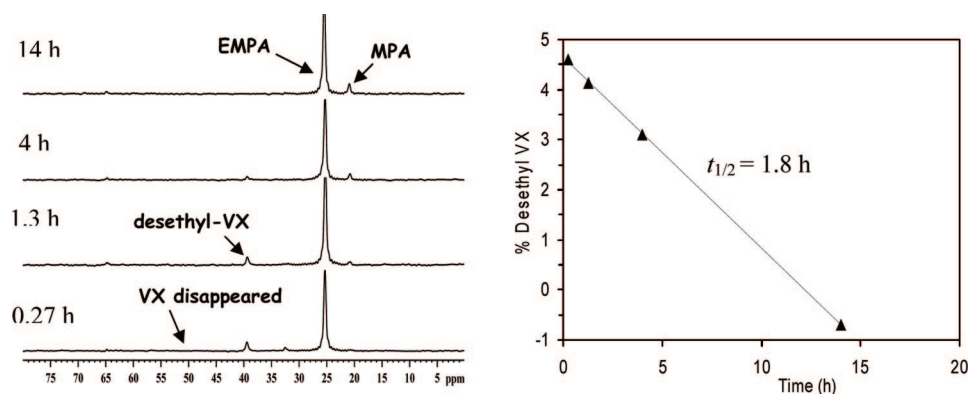


FIGURE 5. Selected ³¹P MAS NMR spectra of adsorbed VX (5 wt %) on AgF/KF/Al₂O₃ (5, 35, H₂O, 160) using H₂O (5%) as an additive (left) and degradation profile for desethyl-VX byproduct onto this adsorbent (right).

KF/Al₂O₃ (20, EtOH, 160) or AgF/KF/Al₂O₃ (5, 35, H₂O, 160) supports is the fastest solid-supported chemical detoxification of VX yet found. One should add that these powders are very simple for preparation using the stable, environmentally benign, and low-cost starting materials alumina and potassium fluoride.

Mechanism. It was concluded by Ando and Clark et al. that organic reactions onto KF/Al₂O₃ might take place by three possible mechanisms: (a) a direct reaction with free active fluoride ion as a strong base, (b) a mechanism in which fluoride ion replaces a hydroxyl group [Al-OH] that cooperatively reacts

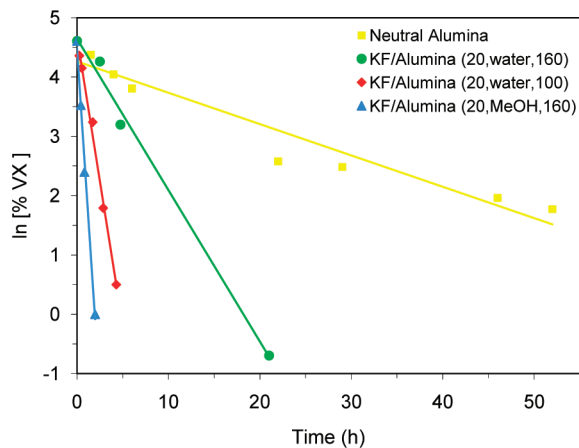
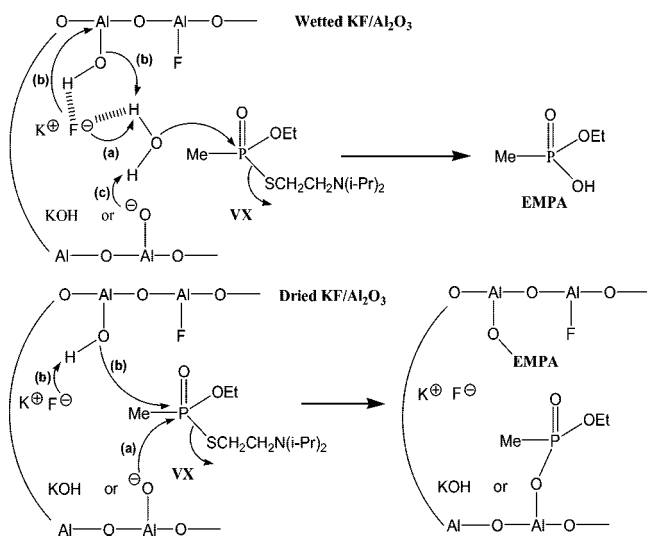


FIGURE 6. Reaction profiles for VX hydrolysis on several KF/Al₂O₃ sorbents.

SCHEME 2



as a strong base, and (c) a reaction with the hydroxide ion according to eq 1 or by [Al–O[−]] when water is added.^{7,10,11} Our observations in the hydrolysis of VX promoted by wetted KF/Al₂O₃ revealed that these three mechanisms might actually be valid, depending on the KF/Al₂O₃ used (Scheme 2, top). Sorbent that was prepared in water and dried in relatively high temperature, such as KF/Al₂O₃ (20, H₂O, 160), did not contain coordinatively unsaturated fluoride ions but KOH and K₃AlF₆, as shown in Figure 2a, and thus, its reaction with VX could comply with mechanism (c) in Scheme 2 (top). Therefore, its performance in the hydrolytic decontamination of VX was close to that of the usual KOH/Al₂O₃. On the other hand, ECUF-KF/Al₂O₃ that was prepared in alcoholic solvents or dried at low temperature, such as KF/Al₂O₃ (20, MeOH, 160), KF/Al₂O₃ (20, EtOH, 160), or KF/Al₂O₃ (20, H₂O, 100), could also react via mechanisms (a) and (b) and therefore might enhance the reactivity of the sorbent.¹⁸ In mechanism (a) HF is formed but immediately reacts with the surface of the alumina support to give K₃AlF₆.¹¹

(18) Recently it was reported by Sandhage and co-workers on a rapid hydrolysis of some nerve agent mimics induced by nanostructural fluorine-doped titania (TiOF₂) under mild conditions (pH 4.5–7.9, 22 °C). However, this transformation is catalyzed by Lewis acidic sites of the solid support. See: Lee, S.-J.; Huang, C.-H.; Shian, S.; Sandhage, K. H. *J. Am. Ceram. Soc.* **2007**, *90*, 1632.

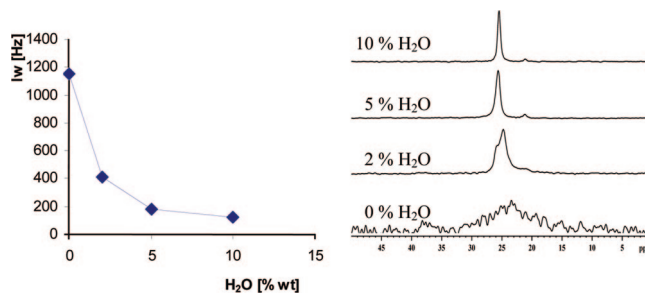


FIGURE 7. (left) The line width (*lw*, in Hz) of the ³¹P-MAS NMR EMPA signals (right) from the KF/Al₂O₃ (40, MeOH, 160) sorbents with different amounts of water.

In the course of our study we have found that KF/Al₂O₃ can chemically destroy VX even in dry conditions in a relatively fast manner. For example, the half-life of VX is only 21 h without the formation of desethyl-VX when subjected to dry KF/Al₂O₃ (40, MeOH, 160), as shown in Table 2 (run 4). Wagner et al. recently reported on the reaction of VX with nanosize-Al₂O₃ and with conventional γ-Al₂O₃.⁴ The reactions were performed without the addition of water to the sorbents. The products were characterized as aluminophosphate compounds, resulting from an attack of aluminum oxide on VX, without the formation of desethyl-VX. We assume that similar to Wagner's results, VX reacts with the aluminum oxide species in dry ECUF-KF/Al₂O₃, to form the corresponding aluminophosphate product (Scheme 2, bottom).

Solid-state MAS NMR experiments of organic compounds adsorbed on an inorganic matrix may differentiate efficiently between mobile or soluble materials to immobile ones. When these compounds are physically but not strongly bound to the matrix, their signals in solid-state MAS NMR will appear as narrow and sharp peaks. On the other hand, when organic compounds react directly with the inorganic matrix, the result of this chemisorption in solid-state MAS NMR may be characterized by broad peaks.^{4a} A confirmation for the formation of soluble and mobile EMPA product in the wetted experiments versus the formation of the rigid aluminophosphate compound in the dry test was obtained by the line width ³¹P-MAS NMR analysis of the processes. Figure 7 shows that the line width of ³¹P-MAS NMR signals of the product obtained by reactions of VX with KF/Al₂O₃ (40, MeOH, 160) was found to be strongly dependent on the percentage of water added prior to the reaction. The product signal at 24.4 ppm in the reaction of VX with dry KF/Al₂O₃ (40, MeOH, 160) was found to be much wider than those of the wetted experiments, and therefore it may result from direct reaction with the basic alumina support. The same tendency was observed in the reaction of VX with AgF/KF/Al₂O₃ (5, 35, H₂O, 160) in the presence of 0, 2%, 5%, and 10% water (Table 3, see also Figures S10–S12, Supporting Information). Nevertheless, we cannot exclude the possibility that this broad signal may partially be attributed to an insoluble EMPA salt (from deprotonation of free EMPA product when the displacement occurred by a hydroxide ion).

Centrifugation Effect by the MAS. Recently we reported that in some protodesilylation reactions using montmorillonite KSF, the rates measured by solid-state MAS ¹H NMR were found to be higher as compared to those measured by solution ¹H NMR of the same reaction mixture.¹⁶ We assumed that these solvent-free processes, in which the diffusion of reactants toward the active sites of the solid support plays a significant role in the reaction kinetics, may be affected by a centrifugation effect

SCHEME 3



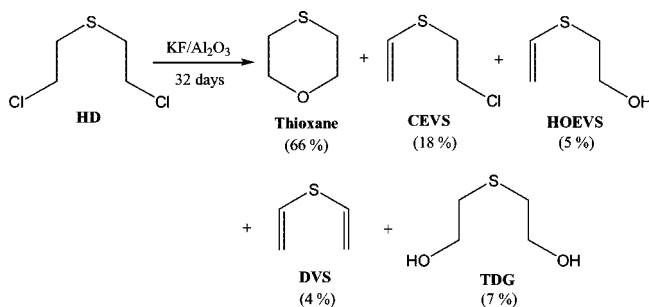
caused by the high spinning rate of the sample (ca. 8000 Hz). In decontamination context it is important to know whether the above-mentioned real-time reaction rates measurements of VX hydrolysis are not affected by the MAS. Therefore, we performed two different examinations on the hydrolysis reaction of VX with $\text{KF/Al}_2\text{O}_3$ (20, H_2O , 160) and $\text{KF/Al}_2\text{O}_3$ (20, MeOH, 160). In one experiment, the hydrolysis rate was tested on two identical samples of wetted (5%) $\text{KF/Al}_2\text{O}_3$ (20, H_2O , 160), when one sample was studied under MAS NMR conditions using 8000 Hz spinning rate and the other sample was measured without spinning. The rates of both reactions were found to be similar. In another experiment, the hydrolysis rate of VX was tested onto a sample of wetted (5%) $\text{KF/Al}_2\text{O}_3$ (20, MeOH, 160) under standard MAS NMR conditions, as mentioned above. Once the concentration of VX was totally decayed, a second sample of this sorbent, that was left aside, was extracted. The reaction time for full conversion of VX measured by the MAS NMR was found to be similar to its counterpart without spinning. Thus, the hydrolysis rates of VX by $\text{KF/Al}_2\text{O}_3$ measured by the MAS NMR technique are indeed results of real-time kinetics. In light of these experiments, we assume that the centrifugation effect observed by us previously is not general for all solid-state organic reactions and is highly dependent on both the reactants and the solid supports used.

Destructive Adsorption of GB (Sarin) on Alumina-Supported Fluoride Reagents. When we tested the reaction of the highly toxic GB on various alumina-supported fluoride powders using water as an additive, the result was immediate hydrolysis ($t_{1/2} < 10$ min). For these experiments GB (5%) was added to wetted (5%) $\text{KF/Al}_2\text{O}_3$ (20, H_2O , 160), $\text{KF/Al}_2\text{O}_3$ (20, MeOH, 160), or $\text{AgF/KF/Al}_2\text{O}_3$ (5, 35, H_2O , 160) supports, without mixing or crushing. After 20–40 min the hydrolysis reactions were completed, so that no starting material or intermediate could be detected. The single product in all cases was isopropyl methylphosphonic acid (IMPA), as emerged from the ^{31}P MAS NMR spectra at ca. 24.0 ppm (Scheme 3, see also Figure S13, Supporting Information). These results are in accordance with the high volatility and the good water-solubility of GB, as well as its susceptibility to basic hydrolytic conditions.

It is well-known that fluoride ion impregnated on alumina reacts as a strong base.^{7,8} Therefore, the reaction of VX with all variations of $\text{KF/Al}_2\text{O}_3$ supports by no means led to the corresponding ethyl sarin product (G-analogue), in opposition to its reaction with neat AgF salt.⁶ In any case, the very high rate of the hydrolysis of GB onto the above-mentioned alumina-supported fluoride powders reveals that even if the undesired G-analogue would partially form during the reaction, it may actually appear as an unstable intermediate.

Detoxification of Sulfur Mustard (HD). Despite the structural simplicity of the blister agent HD (bis-chloroethyl sulfide), its chemistry is abundant and includes some elementary processes such as nucleophilic displacements, eliminations, additions and oxidations, as a function of the reaction conditions.¹⁹ This reactivity arises from the two electrophilic centers activated by the sulfur moiety, relatively acidic protons α to the sulfide group and β to the chlorides, and the nucleophilic

SCHEME 4



feature of the sulfur atom. The high reactivity of HD toward nucleophilic substitutions results from the equilibrium state with its cyclic sulfonium (CS) salt. However, this feature may enhance its environmental stability (in neutral pH) due to the tendency to equilibrate with its toxic sulfonium products such as CH-TDG (vide infra).²⁰ In addition, the oxidation reactions of HD would form the relatively toxic product bis-2-chloroethyl sulfone,²¹ and therefore, hydrolysis processes seem to be favored. These features emphasize the challenge and the importance of a quest for active powders suitable for HD detoxification.

Preliminary results revealed that HD (ca. 7%) reacted with wetted (5%) $\text{KF/Al}_2\text{O}_3$ (20, H_2O , 160) and $\text{KF/Al}_2\text{O}_3$ (20, MeOH, 160) to form several products as shown by the ^{13}C -MAS NMR spectra (Scheme 4 and Figure 8). The spectral picture of the kinetic monitoring was found to be similar for both reactions, and their estimated²² half-life times were 96 and 24 h, respectively. The products peaks were evident for 2-chloroethyl vinyl sulfide (CEVS, 132.3, 113.4, 43.7, 34.7 ppm), divinyl sulfide (DVS, 130.8, 115.4 ppm), 2-hydroxyethyl vinyl sulfide (HOEVS, 133.5, 111.7 ppm, vinylic carbons), thiodiglycol (TDG, 62.1, 35.3 ppm) and 1,4-thioxane (72.0, 33.0 ppm).³ The reaction initiated by a base-catalyzed elimination of HCl or by a substitution reaction of chloride via the CS form, to yield the appropriate monovinyl (CEVS) or chlorohydrin (CH) products, respectively (Scheme 5). The former could undergo two base-catalyzed alternative routes, i.e., another elimination of HCl or a nucleophilic substitution of the remaining chloride that led to DVS and HOEVS, respectively. The CH intermediate could eventually lead to the nontoxic product, 1,4-thioxane (major), by a base-catalyzed intramolecular substitution of the remaining chloride. The small amount of the TDG product (7%) could be a result of the intramolecular versus intermolecular reaction preferred in the heterogeneous conditions that resembles highly diluted reactions. It has to be noted that toxic sulfonium ion product, such as CH-TDG (resulting from a nucleophilic attack of CH intermediate by TDG product),^{3,20} which might be produced in aqueous solutions or less basic solid supports was not detected in our sorbents.

Despite the use of ^{13}C -unlabeled HD in this preliminary study, it was clearly shown that with long acquisition times, the spectral picture of relatively low-rate reactions could be analyzed.

(19) (a) Black, R. M.; Brewster, K.; Harrison, J. M.; Stanfield, N. *Phosphorus, Sulfur Silicon* **1992**, *71*, 31. (b) Black, R. M.; Brewster, K.; Harrison, J. M.; Stanfield, N. *Phosphorus, Sulfur Silicon* **1992**, *71*, 49.

(20) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Ward, J. R. *J. Org. Chem.* **1988**, *53*, 3293.

(21) Yang, Y.-C.; Baker, J. A.; Ward, R. *Chem. Rev.* **1992**, *92*, 1729.

(22) The reactions of HD with $\text{KF/Al}_2\text{O}_3$ supports were performed with unlabeled HD. Therefore, the long acquisition times that were required for the ^{13}C NMR measurements may cause an inaccuracy in their half-life time determination.

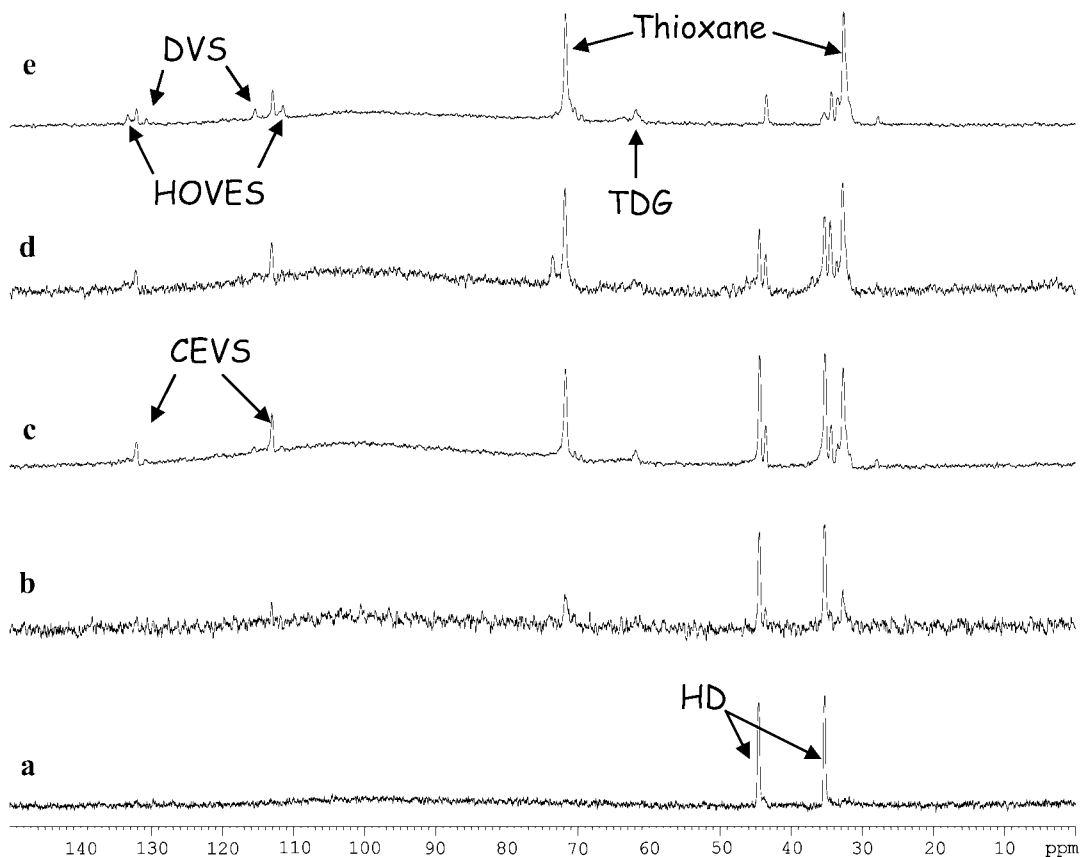
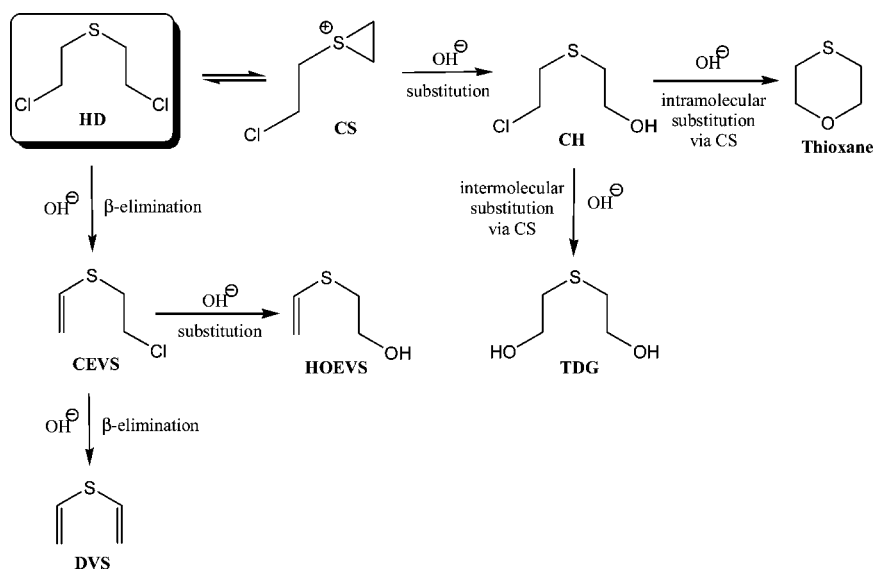


FIGURE 8. Selected ^{13}C MAS NMR spectra of adsorbed HD (5 wt %) on $\text{KF}/\text{Al}_2\text{O}_3$ (20, H_2O , 160) with H_2O (5%) as an additive. Spectra were recorded at (a) 3, (b) 48, (c) 96, (d) 168, and (e) 552 h after sample preparation.

SCHEME 5



However, in order to extend our insights in this process, such as for example studying the effect of Ag^+ ions on its kinetic/products or the influence of water or metal ion content in the solid support, further investigation with ^{13}C -labeled mustard (HD^*) is underway.

Conclusions

The surface area of alumina-supported fluoride reagents such as $\text{KF}/\text{Al}_2\text{O}_3$, $\text{AgF}/\text{KF}/\text{Al}_2\text{O}_3$, and $\text{KF}/\text{Al}_2\text{O}_3$ enriched by so-

called coordinatively unsaturated fluoride ions (termed by us as ECUF- $\text{KF}/\text{Al}_2\text{O}_3$) was found to be very reactive for a hydrolysis-based chemical destruction of VX, GB, and HD. While sarin (GB) reacted instantaneously with these solid supports to yield nontoxic product IMPA, the less reactive CWA VX gave under the same conditions the nontoxic EMPA as a major product (>90%; $t_{1/2}$ range 0.1–6.3 h) together with the toxic desethyl-VX (<10%) byproduct. The latter was further hydrolyzed to the nontoxic MPA product ($t_{1/2}$ range 2.2–161

h). The enhanced activity of wetted ECUF-KF/Al₂O₃ sorbents was related to the free fluoride ions, which act as a strong base. With well-dried alumina-supported fluoride reagents, the reaction with VX proceeded slowly and gave immobile EMPA that was strongly bound to the solid supports. The reactions of HD with both KF/Al₂O₃ and ECUF-KF/Al₂O₃ were found to be slower (estimated $t_{1/2}$ are 96 and 24 h, respectively) and gave the nontoxic product 1,4-thioxane as a major product together with minor amounts of TDG and vinylic compounds. These synthetic and mechanistic studies as well as others^{1–5,15,16} clearly show that the solid-state MAS NMR technique can serve as a powerful tool for real-time study of organic reactions performed on the surface of solid supports. Inter alia we have demonstrated that its unique features such as the capability to differentiate between mobile to immobile components onto the solid surface can efficiently be utilized to probe the mechanism and the products of solid-state organic reactions.

Experimental Section

Materials. KF/Al₂O₃ reagents were prepared by impregnation of KF onto γ -alumina from aqueous or dry alcoholic solutions. For example, KF/Al₂O₃ (20, H₂O, 160) was prepared by dissolving 60 g of KF in water (ca. 400 mL) in a 1 L flask, then 240 g of γ -alumina (neutral) was added, and the bulk of water was removed by evaporation at ca. 90 °C. The powder was dried at 160 °C for 24 h. In cases in which the reaction was performed with wetted solid supports, the appropriate amount of water was added to the powder, which then was crushed for 5 min (using a glass rod) prior to the

addition of CWA. The same procedure was performed in the preparation of AgF/Al₂O₃ and AgF/KF/Al₂O₃.

NMR. ³¹P, ¹³C, and ¹⁹F MAS NMR spectra were obtained at 202, 125, and 471 MHz, respectively, on a 11.7 T (500 MHz) spectrometer, equipped with a 0.4 cm standard CP-MAS probe, using direct polarization (i.e., no cross polarization (CP) was used). Typical spinning rates were 8–10 kHz. Chemical shifts for ³¹P, ¹³C, and ¹⁹F were referenced to external trimethyl phosphate (TMP), TMS, and CFCI₃, respectively, as 0 ppm. For ³¹P spectra the pulse delay was 2 s, which is considered sufficient for relaxation in OP esters on solid matrices. The number of transients per spectrum was 64. For ¹³C spectra the pulse delay was 1 s, and the number of transients per spectrum varied between 20 000 and 100 000. For ¹⁹F spectra pulse delay was 2 s, and the number of transients per spectrum varied between 100 and 1000. For comparison purposes, spectra were recorded under identical conditions.

Sample Preparation. *Caution: These experiments should only be performed by trained personnel using applicable safety procedures.* Samples of the appropriate powder (ca. 40 mg) were added to the 0.4 cm ZrO₂ rotor, and 2–5 μ L of the CWA (VX, GB, or HD) was applied via syringe to the center of the sample. The rotor was sealed with a fitted Kel-F cap. ³¹P and ¹³C MAS NMR spectra were measured periodically to determine remaining starting material and identify degradation products.

Supporting Information Available: Figures S2–S12, ³¹P MAS NMR spectra and reaction profiles of adsorbed VX onto selected KF/Al₂O₃ powders; Figure S13, ³¹P NMR spectra of GB before and after addition to KF/Al₂O₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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