Nanoscale Metal Oxide Particles as Chemical Reagents. Heats of Adsorption of Heteroatom-Containing Organics on Heat-Treated Magnesium Oxide Samples of Varying Surface Areas

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Heats of adsorption (immersion) were measured via a solution calorimeter for a series of heteroatom (oxygen, sulfur, phosphorus) containing organic compounds on thermally activated magnesium oxide (heat treated at 700 °C overnight in vacuo followed by cooling to room temperature). For phosphates, phosphites, and phosphines the heats of adsorption were high and showed a small dependence on substituent effects. For sulfur compounds, –S–H-containing compounds yielded the highest values. For oxygen systems very high heats of adsorption were found for carbonyl compounds. In addition, the strongly basic nature of the MgO surface was demonstrated by the extremely high heats of adsorption/reaction with carboxylic acids. Heats observed for 1-butanol adsorption varied linearly with MgO surface area. Surprisingly, cyclohexane dilution of 1-butanol caused a dramatic lowering of adsorption heats, demonstrating the competitive nature of even such unreactive solvents. The observed heats of adsorption/reaction combined with spectroscopic data allowed some conclusions about the type of surface bonding that took place. The strong interactions of several of these organics demonstrate the nature of heat-treated MgO as a destructive adsorbent for many toxic chemicals. Since MgO is nontoxic and inexpensive and can be prepared in highly surface activated forms, it shows promise for use in air-purification schemes.

Introduction

We have been investigating the preparation and surface activation of high surface metal oxides and consider them as potential reagents for adsorbing and destroying heteroatom-containing organic compounds.[1-5] Recently we have been able to extend our studies to ultrahigh surface area (nanoscale particles) materials.[6,7]

The potential of ionic metal oxides as destructive adsorbents[8] should depend on surface area. The higher the surface area the more reactive surface defects (coordinatively unsaturated ions, cation or anion vacancies) should be available,[2,9-13] and so adsorptive capacity and surface reactivity (affinity) should increase. Indeed, this should be a manifestation of the unusual chemical properties of nanoscale ionic particles.[14]

To obtain more quantitative information about these strong chemisorption processes, we have prepared a series of MgO samples of varying surface area and have measured heats of adsorption of a wide variety of organic compounds. An immediate goal has been to elucidate the mode of these surface interactions. A long-range goal, however, is to develop these oxide reagents for use in air purification.

Results and Discussion

A. Adsorption Process. 1. Physisorption vs Chemisorption. Physisorption is generally characterized by small heats evolved, with several adsorbed layers that are easily removed. Chemisorption, on the other hand, is characterzied by higher heats evolved, monolayer adsorption, and difficulty in removal of the adsorbed species.[15] In our system either process may be allowed,[16] owing to the highly reactive nature of the thermally treated MgO surface. Furthermore, multistep chemisorption processes (chemical reactions) could occur as well, and these might be detected by stepwise evolutions of heat. In fact we have observed such multistep processes occasionally, especially with sulfur- and phosphorus-containing species. However, it is difficult to differentiate between physisorption, chemisorption, and/or multistep chemical reactions. All we can say is that the heats of adsorption observed must be due to physisorption enhanced by chemisorption/chemical reaction processes. And when higher heats of adsorption were observed (and/or multistep evolution of heat), it probably is safe to say that chemisorption/chemical reaction processes are involved.

2. Heats of Immersion vs Heats of Adsorption. Gregg and Sing[16] have shown by means of a thermodynamic model that the heat of immersion ΔH^i (which is evolved when an outgassed, thermally treated solid is immersed in a liquid) is equal or very nearly equal to the net integral heat of adsorption of a vapor by a solid (ΔH^{sv}). Hence, our measured heats (see Experimental Section for more details) are heats of immersion and are taken as

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(1) Lin, S. T.; Klabunde, K. J. *Langmuir*, **1985**, *1*, 600.

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(8) By "destructive adsorbent" we mean a solid reagent capable of such strong surface adsorption of incoming chemicals that the chemical is actually destroying in the process of chemisorption. In other words, irreversible bond breaking takes place.

(9) Nelson, R. L.; Tench, A. J.; Harmsworth, B. J. *J. Chem. Soc., Faraday Trans. 1* **1967**, *63*, 1427

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(16) Gregg, S. J.; Sing, K. S. W. "*Adsorption, Surface Area and Porosity*; Academic Press: London, 1967; Chapter 7, pp 297–305.

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Table I. MgO Samples of Varying Surface Area

MgO sample	S, m^2/g	prep method	ref
1	14	commercial	a
2	130	$Mg(OH)_2$-MgO	13
3	156	ALCO gel	6
4	190	ALCO gel	6
5	253	ALCO gel	6

[a] ROC/RIC Chemical Co., 1988; 99.99% pure.

equivalent to the net integral heats of adsorption. The term "heat of adsorption" is used throughtout this work only for convenience.

3. Effect of Surface Area. Gregg and Sing[16] state that the integral heat of adsorption and the heat of immersion are directly proportional to surface area and are connected with each other by the following equation:

$$\Delta H^{sv} \approx \Delta H^{i} = h^{i}S$$

where ΔH^{sv} can be considered the heat evolved when a vapor adsorbs on a solid, h^i is the heat of immersion per unit area of the solid, and S is surface area. The values of h^i as ΔH^i (or ΔH^{sv}) depend on the history of the solid (i.e., micropores, powder, crystalline, etc.). To measure standard values of h^i, one should use highly dispersed, porous fine powders.

A linear relationship between ΔH^i (or ΔH^{sv}) and S usually requires the absence of strong chemisorption processes[17] or at least requires that different surface area solids interact with the adsorbate in the same way. If strong chemisorption processes are involved, it might be expected that higher surface area solids (with more and possibly different types of defect sites) would chemisorb somewhat differently. Thus, a nonlinear relationship could be realized.

We have studied the relationship between surface area and ΔH^{sv} for 1-butanol and cyclohexanone adsorption. A series of MgO samples were prepared in different surface area forms, as summarized in Table I. Each was heat treated and handled in the same way prior to immersion in 1-butanol or cyclohexanone. Figure 1 shows this relationship for 1-butanol, and a good linear plot was obtained. Figure 2 shows the same relationship for cyclohexanone, and some deviation from linearity, although small, is evident. Since cyclohexanone yields a larger ΔH^{sv} value, this deviation suggests that a stronger chemisorption process is occurring. On the other hand, since large deviations were not encountered, we can conclude that *surface* chemisorption is occurring and not processes where the crystallites are being broken up and consumed (a *surface* stoichiometric reaction is occurring rather than a complete stoichiometric reaction).

We do not attribute these findings to a pure physisorption process for 1-butanol since it is known that dissociative chemisorption occurs with alcohols on single-crystal MgO.[18] This information, combined with the fact that the heats of adsorption do not rise faster than linearly (for 1-butanol) makes it evident that special types of defect sites are not necessary for O–H dissociation on MgO.[19]

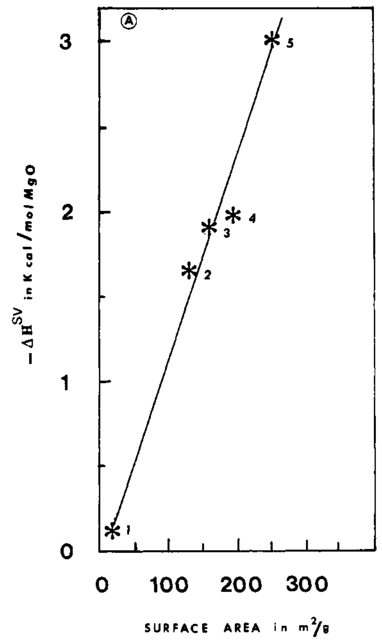

Figure 1. Relationship between surface area and heat of adsorption for 1-butanol/MgO systems. The numbers 1–5 refer to different MgO samples described in Table I.

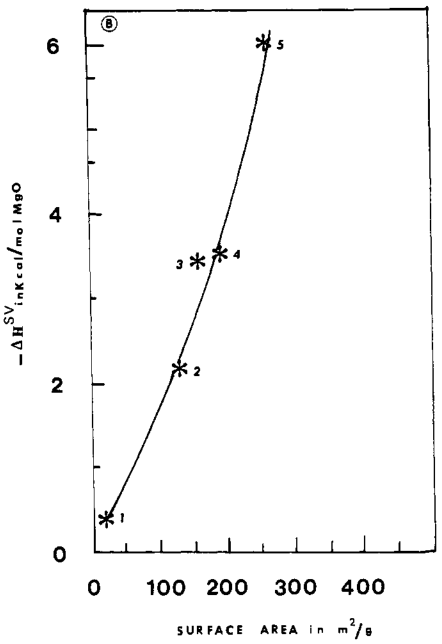

Figure 2. Relationship between surface area of MgO and heats of adsorption for cyclohexanone. The numbers 1–5 refer to different samples of MgO as described in Table I.

4. Steric Effects on Alcohol Adsorption. An interesting feature of alcohol adsorption is its sensitivity to steric effects. A homologous series of primary straight-chained alcohols 1-butanol through 1-dodecanol alcohol (C_4–C_{12}) were allowed to adsorb on 130 m^2/g MgO (see Figure 3). Moving from 1-butanol to 1-pentanol caused a significant decrease in the observed heat of adsorption. From C_6 to C_{12} ΔH continued to decrease, although much more slowly. It would appear that the strength of interaction of the –OH group with the surface is significantly affected by the dangling alkyl group. Thermal motion of the longer chains must weaken the interaction as well as allow fewer ROH molecules to approach the surface for chemisorption. A similar effect was reported by Takezawa and Kobayashi,[20] who found through spectroscopic studies that the strength of the Mg^{2+} interaction with the O–H group of the alcohol decreased with increasing chain length.

5. Solvent Dilution Effects. Our results showed that heats of adsorption are also quite sensitive to solvent di-

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[18] Martinez, R.; Barteau, M. A. *Langmuir* **1985**, *1*, 684.

[19] For dissociation of C–H bonds special sites are necessary: Hoq, M. F.; Nieves, I.; Klabunde, K. J. *J. Catal.* **1990**, *123*, 349.

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Table II. Heats of Adsorption (Immersion) for Various Compounds over Heat-Treated MgO

compd	ΔH^{sv}, kcal/mol of MgO	*T*, °C	$(\Delta H^{sv})_{corr}$,[a,b] kcal/mol of MgO at 25 °C
1. cyclohexane	-0.16	23.436	-0.090
2. *N,N*-dibutylformamide	-0.24	24.656	*c*
3. benzaldehyde	-2.36	23.897	-1.23
4. hexahydrobenzaldehyde	-4.19	24.510	*c*
5. pentanal	-5.11	24.278	-3.02
6. cyclohexanone	-2.61	24.187	-1.45
7. water	-2.16	23.617	-2.16
8. 1-butanol	-1.69	24.010	-1.12
9. 1-pentanol	-1.09	24.197	-0.71
10. 1-hexanol	-0.95	23.530	-0.61
11. 1-heptanol	-0.94	23.797	-0.63
12. 1-octanol	-0.98	24.219	-0.65
13. 1-nonanol	-0.93	24.453	*c*
14. 1-decanol	-0.95	24.266	-0.63
15. 1-undecanol	-0.92	24.416	-0.62
16. dodecanol	-0.94	24.177	-0.64
17. pentanoic acid	-9.28	24.689	-5.59
18. cyclohexanecarboxylic acid	-1.92	24.147	*c*
19. thiophenol	-2.14	23.948	-1.09
20. dibutyl sulfide	-0.69	26.838	-0.040
21. cyclohexanethiol	-0.63	24.808	-0.16
22. thiooxane	-1.35	24.131	*c*
23. triethyl phosphite ($(C_2H_5O)_3P$)	-1.35	24.901	*c*
24. tris(2-chloroethyl) phosphite ($(ClCH_2CH_2O)_3P$)	-1.59	23.423	*c*
25. triisopropyl phosphite ($((CH_3)_2CHO)_3P$)	-1.09	24.537	*c*
26. triphenyl phosphite ($(PhO)_3P$)	-1.83	23.767	*c*
27. triethyl phosphate ($(C_2H_5O)_3P{=}O$)	-1.19	24.452	*c*
28. trimethyl phosphate ($(CH_3O)_3P{=}O$)	-0.92	24.120	*c*
29. dimethylmethyl phosphonate	-1.89	24.947	*c*
30. tri-*n*-butylphosphine ($(n\text{-}C_4H_9)_3P$)	-1.06	24.948	*c*

[a] From corrected values, one can deduce the following: the correction does affect the overall magnitude of ΔH^{sv}, but it does not affect the trend among the various functional groups. [b] From corrected values, one can deduce the following: $(\Delta H^{sv})_{corr}$ is about 50% of the values obtained from ΔH_T. This is due to the fact that most of the heat capacities of the organic chemicals are about half the heat capacity of water (at 25 °C and for 100 g). [c] No available heat capacity and thus $(\Delta H^{sv})_{corr}$ cannot be calculated.

lution, even when a supposedly nonreactive solvent such as cyclohexane is employed. Thus, as shown in Figure 4, dilution of 1-butanol by cyclohexane progressively caused large decreases in observed heats of adsorption. It is evident that cyclohexane itself does not yield a large ΔH^{sv}. However, its presence in increasing amounts clearly affects 1-butanol adsorption. This effect might be attributed to cyclohexane competition for active sites and could mean that cyclohexane does interact more strongly with the surface than might be anticipated. (It should be noted here that alkanes are known to undergo H–D exchange in the presence of D_2 over MgO, but the rate of this process is quite slow at room temperature.[19] Also, it is known that thermally treated MgO dissociatively adsorbs small amounts of methane even below room temperature.[21] However, the fact remains that ΔH^{sv} for cyclohexane itself is quite low, and so a true competition of cyclohexane with 1-butanol seems rather unlikely. Therefore perhaps a better explanation would deal with entropy changes. Thus, as 1-butanol is diluted in cyclohexane, entropy changes would be more and more positive. But in the presence of large amounts of cyclohexane, when 1-butanol becomes surface adsorbed, entropy change would become progressively more negative as the 1-butanol became more and more dilute. More order would be created out of disorder for the more dilute solutions, and this could greatly affect the Gibbs free energy ΔG (as reflected in ΔH^{sv}).

Actually, these results may have significance for other systems where organized layers are formed on surfaces. Dilution effects forcing larger than expected entropy changes upon adsorption might be useful as a tool in understanding such systems better.

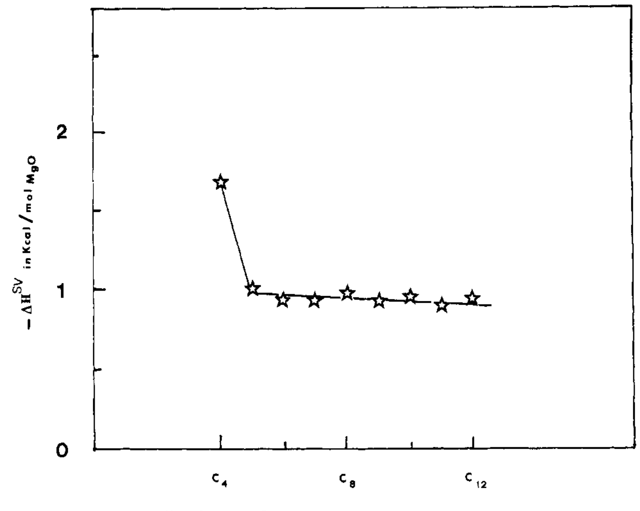

Figure 3. Relationship between heats of adsorption and length of carbon chain for primary, straight-chained alcohols on thermally treated MgO (130 m^2/g).

B. Survey of Heteratom Organic Compounds. 1. Introduction. A survey of functional groups was necessary, and Table II summarizes the heats of adsorption that we obtained for a long series of heteratom-(O, S, P) containing organic compounds. Note that for the compounds with known heat capacities, a corrected ΔH^{sv} value is given. The correction was necessary since the calorimeter was calibrated on the basis of a water-solvated standard. Since the heat capacity of water is approximately twice that of most organics, the correction is significant. However,

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(21) Ito, T.; Toshihiko, T.; Kawasaki, M.; Miyazawa, K.; Hamada, E.; Toi, K. *Proceedings of First Tokyo Conference on Advances in Catalysis Science and Technology*, July 1–5, 1990; Catalysis Society of Japan; p 209.

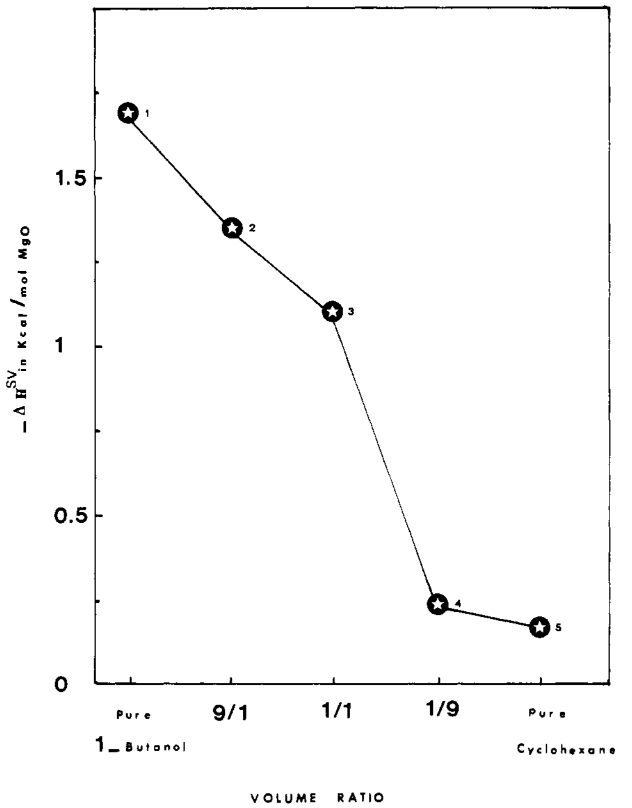

Figure 4. Effect of cyclohexane solvent in heats of adsorption of 1-butanol: (1) pure 1-butanol; (2) 9/1 1-butanol/cyclohexane; (3) 1/1 1-butanol/cyclohexane; (4) 1/9 1-butanol/cyclohexane; (5) pure cyclohexane.

trends in heats of adsorption were not affected much since the organics all have similar heat capacities.

Also note that the heats of adsorption are reported per mole of MgO. Of course, to get a more realistic value for the strength of the adsorbate–adsorbent interaction, only the surface MgO moieties should be considered. Since this survey work was done using 130 m^2/g MgO, it can be calculated that about 1 of 10 MgO moieties is on the surface.[22] Thus, the true ΔH^{sv} values for the surface interaction are about 10 times the values listed in Table II.

2. **Oxygen-Containing Compounds.** Let us consider the oxygen-containing compounds first. Aldehydes were adsorbed strongly. Pentanal, with few steric restrictions and the presence of α-H groups, adsorbed most strongly. It is known that the basic surface of MgO can cause base condensation reactions of aldehydes:[23]

$$RCH_2CHO \xrightarrow{MgO} RCH_2CH(OH)CHRCHO$$

Further reactions are also possible, such as polycondensations and dehydration.[2] Such reactions are apparently reflected in the heats of adsorption (reaction) observed. In the same light it is interesting to compare benzaldehyde and hexahydrobenzaldehyde. In the latter case, where an α-H group is present, a much higher heat of adsorption was observed. Still, benzaldehyde did adsorb strongly, and it is known that Cannizzaro-like reactions can take place on MgO and CaO:[24]

$$C_6H_5CHO \xrightarrow{MgO} C_6H_5C(O)OCH_2C_6H_5$$

One other aldehyde, *N,N*-dibutylformamide, exhibited only a small heat of adsorption. Apparently surface reactions did not occur in this case, and only weak chemisorption or physisorption took place. Most likely electronic effects, lessening the electrophilic character of the carbonyl group, play a deciding role in this case.[25]

One ketone, cyclohexanone, was studied in some detail, as discussed earlier. Strong adsorption is apparent, and this probably reflects surface chemisorption and condensation reactions similar to aldehydes.[2]

A carboxylic acid, *n*-pentanoic acid, was also studied, and a huge heat of adsorption was realized. An efficient and very exothermic dissociative chemisorption is evident here and reflects the exothermicity of a strong base–strong acid interaction.[26] Organic acids undergo dissociative chemisorption efficiently even on single crystals of MgO, such as the surface of oxidized Mg(001).[18] Moreover, Garrone and Stone report analogous findings on microcrystalline MgO.[27] So we can be confident that pentanoic acid strongly dissociatively adsorbs on our MgO sample. We suspect that the nanoscale MgO particles are being broken up so that a more nearly stoichiometric reaction takes place, judging from the very high heat of adsorption. Also, compare the much lower heat of adsorption for cyclohexane carboxylic acid (Table II) where, perhaps due to steric effects, the chemisorption process is restricted to surface interaction without crystallite breakup.

Finally, for oxygen compounds, let us return to alcohols. As mentioned earlier, a series of straight-chained alcohols were compared. Of those studied, 1-butanol adsorbed most strongly, and it is known that for C_1 and C_2 alcohols this occurs by a dissociative chemisorption process where the RO^- group attaches to Mg^{2+} and H^+ attached to O^{2-}.[18] Note, however, that the overall heats of adsorption were considerably lower than those observed for aldehydes and ketones (where base condensation reactions also take place). On the other hand, Kagel and Greenler[17] report that alcohols generally physisorb at room temperature but undergo chemisorption at higher temperatures. On the basis of this background and the significant lowering of heats of adsorption as the alcohol chain length grows, we believe that dissociative chemisorption is the mode of interaction at room temperature on our MgO samples for the smaller alcohols up through *n*-butanol. The higher alcohols, due to steric problems, probably switch to a physisorption mode.

3. **Sulfur-Containing Compounds.** The heats of adsorption for sulfur compounds present some interesting results. Note that thiophenol yielded nearly 4 times the heat of adsorption as cyclohexanethiol. Here acidity appears to play an important role where thiophenol is acidic enough for dissociative chemisorption,[28] while cyclohexanethiol apparently only physisorbs. Steric effects may also play a role but probably a less decisive one. Another interesting comparison is with the thioethers dibutyl sulfide and thioxane, the former showing a much lower heat of adsorption. It seems likely in the case of thioxane that both the sulfur and oxygen atoms chemisorb on Mg^{2+} sites, giving an overall more exothermic process, while for dibutyl sulfide only one functional group is available for such adsorption.

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(28) Tanabe, K. *Catalysis by Acids and Bases*; Elsevier Scientific: New York, 1977; p 4.

4. **Phosphorus-Containing Compounds.** In the case of phosphorus compounds moderate to high heats of adsorption were realized. The functionality on phosphorus made some difference, although slight. Thus, phosphates and phosphites fell in the same range, 1.1–1.9 kcal/mol of MgO, while the phosphine was nearly 1.1 kcal/mol of MgO.

Among the phosphites, substituent effects play a role, and the trend found was RO– = C_6H_5O– > $ClCH_2CH_2O$– > CH_3CH_2O– > $(CH_3)_2CHO$–. It appears that steric effects have a moderate influence since the isopropyl phosphite gives the lowest value. In the case of phosphites we can also make a rough comparison of adsorption amount vs heats of adsorption. In earlier work we found that the order for amount adsorbed was RO– = CH_3CH_2O– > $ClCH_2CH_2O$– > $(CH_3)_2CHO$–,[1] and therefore, the $ClCH_2CH_2O$– derivative shows a higher heat of adsorption than might be predicted from the amount adsorbed. On the basis of the decomposition products observed, it is apparent that $ClHC{=}CH_2$ is readily eliminated with this system. Perhaps the higher than expected heat observed is due to adsorption of this secondary product as well.

The phosphates offer an interesting case. Earlier spectroscopic work showed that the P=O bond is essentially destroyed on adsorption.[1] Decomposition products are readily formed, and adsorption of secondary products may explain why triethyl phosphate showed a higher overall heat of adsorption than trimethyl phosphate. In the case of dimethylmethyl phosponate (DMMP) the highest heat of adsorption was observed. This molecule differs from trimethyl phosphate by only one CH_3 group

$(CH_3O)_3P{=}O$	$(CH_3O)_2P(CH_3){=}O$
trimethyl phosphate	DMMP

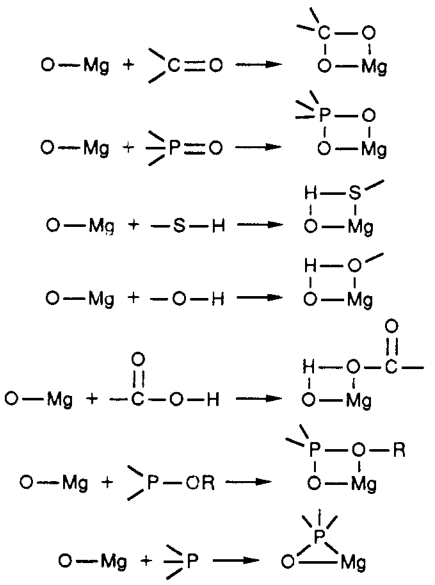
and yet exhibits approximately twice the heat of adsorption. It would appear that DMMP may possess a facile mode of decomposition; perhaps adsorption of secondary products is also contributing here. Since DMMP serves as a good model of toxic phosphorus compounds, we are currently investigating the adsorption/decomposition process in some detail.[7] Actually, DMMP has already been the target of similar intensive studies such as on silica,[29] alumina,[30,31] and α-Fe_2O_3.[29]

It seems clear that the heats of adsorption we observe are mainly due to chemisorption (sometimes dissociative). As a further check on this, we attempted to correlate dipole moments of phosphorus compounds[32] with ΔH^{sv}. No correlation was found, again indicating that pure physisorption cannot be the predominant mode of interaction.

The probable mechanisms of adsorption and decomposition of organophosphorus on heat treated MgO have been discussed previously.[1] These data on heats of adsorption further emphasize the facility and exothermicity of these processes.

5. **Summary of Functional Groups Studies.** The surface of heat-treated MgO adsorbs a variety of functional groups with the evolution of considerable amounts of heat. Acid adsorption/reaction is, as might be expected, extremely exothermic. Beyond that we note that carbonyl groups also adsorb very exothermically. These are followed by phosphorous compounds, some sulfur compounds, water, and small alcohols. Exothermicity for larger alcohols is considerably smaller.

Scheme I



Based on earlier spectroscopic data as well as these results, generalized chemisorption schemes for these functional groups are shown in Scheme I. However, since in only a few cases have spectroscopic data been collected and amounts adsorbed determined along with ΔH^{sv}, it is difficult to conclude much about mechanistic details.

Overall Summary

Many functional groups adsorb exothermically on heat-treated MgO. Strong chemisorptive processes, usually dissociative, are common. These processes are usually directly dependent on surface area and can be influenced by steric effects. Facile dissociation/decomposition processes can contribute to heats of adsorption due to the adsorption of secondary products. Particularly interesting cases along this line are halogen substituted phosphorus compounds and DMMP.

Experimental Section

Calorimeter. A Parr 1451 solution calorimeter was used, calibrated and operated as described by the manufacturer.

Calculations of the Heats of Adsorption. After immersion of the sample of MgO in the liquid organic compound, a plot of temperature vs time was obtained. The corrected temperature rise ΔT_c was obtained by extrapolation, and the heat of adsorption (or immersion) calculated as

$$Q = e\Delta T_c$$

where Q = the energy change in calories, e = the energy equivalent of the calorimeter and its contents per °C (=127.27 cal/°C based on the calorimeter calibration using TRIS/HCl/H_2O), and ΔT_c = the corrected temperature rise in °C.

After deduction of the value of Q, the heat of adsorption in a liquid phase could be calculated as follows:

$$\Delta H^{sv}{}_{0.63R} = -\frac{Q}{m}\frac{M}{1000}$$

where $\Delta H^{sv}{}_{0.63R}$ = the heat of adsorption from liquids in kcal/g of MgO at the temperature at the $0.63R$ point on the thermogram, m = the weight of MgO in grams, and M = molecular weight of MgO, yielding $\Delta H^{sv}{}_{0.63R}$ in kcal/mol of MgO.

MgO Preparation. Methods of preparation have been described earlier, and references are given in Table I.

MgO Activation. 0.2–0.5 g of MgO was activated in the vacuum by pumping down to 10^{-6} Torr and slowly heating to 700 °C (i.e., the desired activation temperature for all samples) and

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(32) McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman: San Francisco, 1963.

held overnight (~14 h), followed by slow cooling to room temperature. The pumping was maintained during the entire heat-treatment activation process.

Typical Measurement of Heat of Adsorption and Calorimeter Calibration. Activated MgO (0.2–0.5 g cooled to room temperature) was placed in the Teflon dish that was then attached to the glass sample cell. Manipulations were carried out under nitrogen as much as possible. Organic liquid (100 g; phosphorus-, sulfur-, or oxygen-containing organics dried over molecular sieves (4A)) was placed in the glass Dewar. After thermal equilibration between reactants (solid and liquid), the push rod was depressed to immerse the Teflon dish containing the MgO in the excess organic liquid. The adsorption proceeded under continuous stirring. The temperature change was then recorded by a thermistor and read from a bridge inside the calorimeter case. Changes in temperature were traced by a potentiometric strip chart recorder to produce a thermogram from which the heat of adsorption could be calculated as mentioned above. It is important to mention here that the calorimeter needs calibration prior to the measurements. TRIS/HCl as aqueous standard was used for this calibration. The procedure for the calibration is very similar to that of measurement. Exactly 0.5 g of TRIS (tris(hydroxymethyl)aminomethane) was placed in the Teflon dish, and exactly 100 g of aqueous of 0.1 N HCl was placed in the glass Dewar. Afte thermal equilibration, the push rod was depressed to immerse TRIS in the HCl, and a typical thermogram was then recorded. From this thermogram, the energy equivalent in cal/°C is calculated according to a given calculation by the calorimeter manufacturer. With help of the calculated energy equivalent, the heat of adsorption could be obtained as mentioned previously.

It is important here to note that this standardization is based on aqueous solution. However, in our experiments organic liquids were used. Therefore, a correction is needed. Detailed information about this correction can be found in the Appendix.

Appendix

A correction was needed to obtain the net integral heats of adsorption based on the heat capacities of the organic compounds. The correction is as follows:

$$e = c_{\mathrm{p(aq)}} + c_{\mathrm{p(inert)}}$$

where e = the energy equivalent of the calorimeter and its content in cal/°C (=127.27 cal/°C from the calorimeter calibration TRIS/HCl), $c_{\mathrm{p(aq)}}$ = the heat capacity of the aqueous solution of TRIS/HCl, which turns out to be the heat capacity of water at room temperature in very close approximation and equal to 99.828 cal/°C for 100 g of water, $c_{\mathrm{p(inert)}}$ = the heat capacity of calorimeter contents (cables, glass Dewar, glass sample cell, etc.), and $c_{\mathrm{p(inert)}} = 127.27 - 99.828 = 22.442$ cal/°C. The corrected energy equivalent of the calorimeter and its contents is defined as follows:

$$e' = c_{\mathrm{p(organic)}} + c_{\mathrm{p(inert)}}$$

where $c_{\mathrm{p(organic)}}$ = the heat of capacity of the organic compound used and taken from the ref 33.

Note that all $c_{\mathrm{p(organic)}}$ values are taken at room temperature (25 °C) for 100 g of the organic compound. The corrected net integral heat of adsorption $(\Delta H^{\mathrm{sv}})_{\mathrm{corr}}$ is then

$$(\Delta H^{\mathrm{sv}})_{\mathrm{corr}} = \frac{e'(\Delta T_{\mathrm{c}})}{1000m} M$$

where e' = the corrected energy equivalent in cal/°C for each individual organic compound, ΔT_{c} = the corrected temperature rise obtained from the diagram recorded by the recorder for each organic compound/MgO system, m = mass of MgO in grams, and M = molecular weight of MgO (40.30 g/mol).

We calculated $(\Delta H^{\mathrm{sv}})_{\mathrm{corr}}$ for all compounds with known heat capacities, and they are listed in Table II.

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Registry No. C_6H_5CHO, 100-52-7; $(C_2H_5O)_3P$, 122-52-1; $(ClCH_2CH_2O)_3P$, 140-08-9; $((CH_3)_2CHO)_3P$, 116-17-6; $(PHO)_3P$, 101-02-0; $(C_2H_5O)_3P{=}O$, 78-40-0; $(CH_3O)_3P{=}O$, 512-56-1; $(n\text{-}C_4H_9)_3P$, 998-40-3; MgO, 1309-48-4; cyclohexane, 110-82-7; *N,N*-dibutylformamide, 761-65-9; hexahydrobenzaldehyde, 2043-61-0; pentanal, 110-62-3; cyclohexanone, 108-94-1; water, 7732-18-5; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; 1-nonanol, 143-08-8; 1-decanol, 112-30-1; 1-undecanol, 112-42-5; 1-dodecanol, 112-53-8; pentanoic acid, 109-52-4; cyclohexanecarboxylic acid, 98-89-5; thiophenol, 108-98-5; dibutyl sulfide, 544-40-1; cyclohexanethiol, 1569-69-3; thioxane, 57917-36-9; dimethyl methyl phosphonate, 756-79-6.

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(33) Domalski, E. S.; Evans, W. H.; Hearing, E. D. *Heat Capacities and Entropies of Organic Compounds in the Condensed Phase*; Published by American Chemical Society and the American Institute of Physics for National Bureau of Standards: New York, 1984.