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A study of complexation of chloral hydrate with heteropoly anions having various structures

G. M. Maksimov,★ M. N. Timofeeva, and V. A. Likholobov

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
5 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (3 832) 34 3056. E-mail: root@catalysis.nsk.su

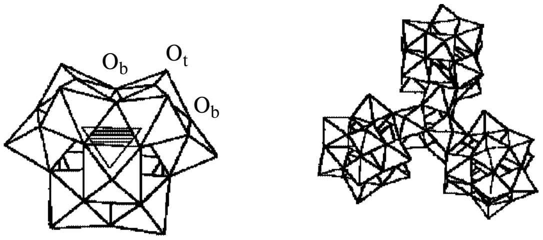
^{1}H NMR was applied to study the interaction of chloral hydrate in deuterionitrobenzene solution with tetrabutylammonium salts of the heteropoly acids (HPA) belonging to five structural types: Keggin ($H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$), Dawson (α-$H_6P_2W_{18}O_{62}$, α-$H_6P_2Mo_{18}O_{62}$, α-$H_4S_2Mo_{18}O_{62}$), $H_6P_2W_{21}O_{71}(H_2O)_3$, $H_6As_2W_{21}O_{69}(H_2O)$, and $H_{21}B_3W_{39}O_{132}$. The surface of the HPA anions is nonuniform in acid-base properties. A general rule for all HPA was found, namely, that the HPA acidity increases with a decrease in the specific anion charge (per W or Mo atom).

Key words: heteropoly acids, acidity, basicity, ^{1}H NMR.

In recent years, considerable attention has been paid to the use of heteropoly acids (HPA) in acid catalysis.[1—4] In this connection, the acidity of HPA has been studied by various physicochemical methods[2,5] including comparison of the basicities of the HPA anions. These data can be gained from ^{1}H NMR study of complexation between an anion and a geminal diol, 1,1-dihydroxy-2,2,2-trichloroethane (chloral hydrate) in organic media.[6,7] This reaction is assumed[6] to yield complexes with two hydrogen bonds involving only bridging (O_b) but not terminal (O_t) oxygen atoms of the heteropoly anion (Fig. 1). The chemical shifts of the hydroxyl protons of chloral hydrate increase in parallel with the increase in the basicity of the anion, or, in other words, with the decrease in the acidity of the corresponding HPA. The application of this method for HPA having similar structures (Keggin acids) resulted in the following acidity series[7]:

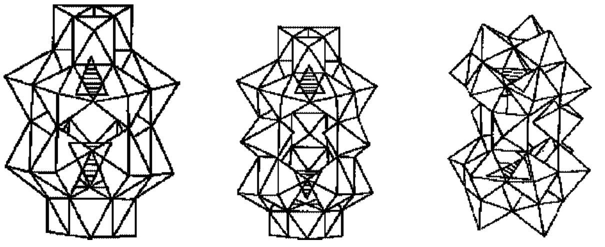
$$H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} \approx$$
$$\approx H_4GeW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_4GeMo_{12}O_{40}.$$

This series corresponds to the theoretical views[2] according to which the acidity of HPA having similar structures should decrease with an increase in the charge of the HPA anion and W-HPA are usually more acidic than Mo-HPA.[1,2]



α-$PM_{12}O_{40}^{3-}$
(Keggin anion)

$B_3W_{39}O_{132}^{21-}$



α-$P_2M_{18}O_{62}^{6-}$
(Dawson anion)

$P_2W_{21}O_{71}(H_2O)_3^{6-}$

$As_2W_{21}O_{69}(H_2O)^{6-}$

Fig. 1. Structures of heteropoly anions (M = Mo, W).

In this study, complex formation of chloral hydrate with the HPA anions belonging to five structural types, namely, Keggin ($H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$), Dawson (α-$H_6P_2W_{18}O_{62}$, α-$H_6P_2Mo_{18}O_{62}$, α-$H_4S_2Mo_{18}O_{62}$), $H_6P_2W_{21}O_{71}(H_2O)_3$, $H_6As_2W_{21}O_{69}(H_2O)$, and $H_{21}B_3W_{39}O_{132}$ was studied by ^{1}H NMR spectroscopy in a solution in deuterionitrobenzene.

Experimental

Chloral hydrate (Fluka, 99%) and deuterionitrobenzene (State Institute of Applied Chemistry, Russia, 99.7%) were used as received. HPA (except $H_4S_2Mo_{18}O_{62}$) were synthesized and identified using procedures reported previously.[5] Tetrabutylammonium (TBA) salts of HPA were precipitated from aqueous solutions of HPA by stoichiometric amounts of TBA bromide. The resulting salts were purified by reprecipitation with water from solutions in acetonitrile and dried at 150 °C to give anhydrous salts. The TBA salt of the $H_8CeMo_{12}O_{42}$ HPA could not be prepared by this method. The identity of the anions in the initial HPA and in their TBA salts was checked by IR spectroscopy. The ^{11}B and ^{31}P NMR spectra of solutions of the TBA salts of $B_3W_{39}O_{132}^{21-}$ and phosphorus-containing

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Table 1. Signals from the OH groups in chloral hydrate in the ^{1}H NMR spectra of solutions in the presence of HPA salts

Salt	[Salt] /mmol L^{-1}	δ ($\Delta\nu_{1/2}$/Hz)
Without salt	—	0.82 (12)
$TBA_{3,0}PW_{12}O_{40}$	10	4.83 (14)
	20	4.84 (12)
	30	4.83 (14)
$TBA_{4,0}SiW_{12}O_{40}$	10	4.96 (20)
	20	5.05 (20)
	30	5.11 (14)
$TBA_{3,0}PMo_{12}O_{40}$	10	4.88 (12)
	20	4.91+4.88* (general 12)
	30	4.92+4.89* (6+6)
$TBA_{4,0}S_2Mo_{18}O_{62}$	10—30	4.82 (18)
$TBA_{5,6}H_{0,4}P_2W_{18}O_{62}$	10	5.34+5.36* (general 12)
	20	5.58+5.61* (general 14)
$TBA_{5,2}H_{0,8}P_2Mo_{18}O_{62}$	10	5.50 (100)
	20	5.70 (100)
	30	6.00 (100)
$TBA_{5,65}H_{0,35}P_2W_{21}O_{71}(H_2O)_3$	10	6.35+6.61+6.82** (14+20+40)
	20	6.30+6.70+6.96** (14+20+40)
$TBA_{6,0}As_2W_{21}O_{69}(H_2O)$	10	5.60+6.00+6.21** (40+30+40)
	20	5.61+5.95+6.23** (40+20+40)
$TBA_{11,0}H_{10}B_3W_{39}O_{132}$	5	5.51+5.61+5.75* (7+10+12)
	10	5.46+5.72+5.81* (7+10+12)
	15	5.42+5.70+5.85* (7+7+10)

* Signals with equal intensities.

** The mutual signal intensity is difficult to estimate due to their overlap.

anions in $C_6D_5NO_2$ in the presence of chloral hydrate demonstrated the presence of unchanged $B_3W_{39}O_{132}{}^{21-}$, $PW_{12}O_{40}{}^{3-}$, $PMo_{12}O_{40}{}^{3-}$, and $P_2W_{21}O_{71}(H_2O)_3{}^{6-}$ anions and β- and γ-isomer impurities in amounts of 8—10% in the α-$P_2W_{18}O_{62}{}^{6-}$ and α-$P_2Mo_{18}O_{62}{}^{6-}$ samples.

Free $H_4S_2Mo_{18}O_{62}$ is unknown; however, this HPA exists as tetraalkylammonium salts.**[8,9]** We prepared the TBA salt by the procedure reported**[9]** for the synthesis of the tetraethylammonium salt of $S_2Mo_{18}O_{62}{}^{4-}$. In this case, TBA bromide was used for precipitation. This salt was purified in the same way as other TBA salts of HPA. The IR spectrum of TBA—$S_2Mo_{18}O_{62}{}^{4-}$ corresponds to the spectrum of the tetraethylammonium salt of this HPA.**[9]**

The amount of the TBA cation in the salts was determined from the mass loss after annealing for 1 h at 600 °C. The compositions of the salts are listed in Table 1. In the text, the HPA are given in an abridged form, for example, PW_{12}, S_2Mo_{18}, and so on. The attempts to prepare completely substituted α-P_2W_{18}, α-P_2Mo_{18}, and P_2W_{21} salts by adding a calculated amount of a methanolic solution of TBA to an acetonitrile solution of the salt resulted in partial hydrolysis of the anions (observed in the ^{31}P NMR spectra), while re-precipitation with the addition of water produced again partially substituted salts.

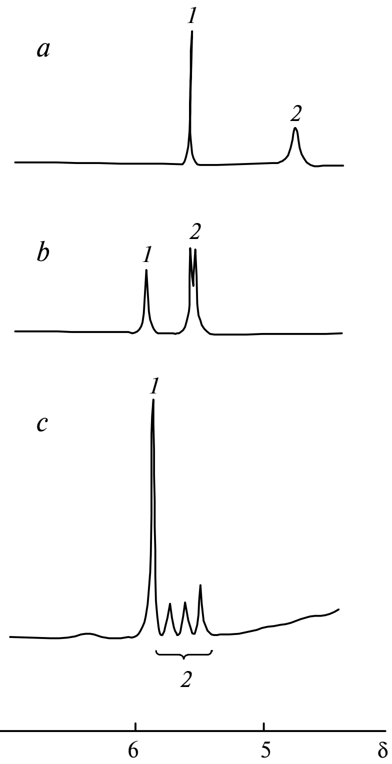

Fig. 2. ^{1}H NMR spectra of solutions of HPA salts in $C_6D_5NO_2$ in the presence of chloral hydrate: (*a*) PW_{12} (10 mmol L^{-1}), (*b*) P_2W_{18} (10 mmol L^{-1}), (*c*) B_3W_{39} (5 mmol L^{-1}), (*1*) signals of the CH protons in $Cl_3CCH(OH)_2$; (*2*) signals of the OH protons in $Cl_3CCH(OH)_2$.

The degree of interaction of chloral hydrate with the HPA anions was estimated from a change in signals in the 4—7 ppm region of the ^{1}H NMR spectra of freshly prepared solutions of chloral hydrate (0.0138 *M*) in $C_6D_5NO_2$ containing admixtures of the TBA HPA salts (Fig. 2). Tetramethylsilane was used as the internal standard. Solutions contained ≤0.03% (w/w) water introduced into the system together with the initial chloral hydrate and deuterionitrobenzene.

The ^{1}H, ^{31}P, and ^{11}B NMR spectra were recorded on a Bruker MSL-400 spectrometer operating at 100.61, 161.98, and 128.36 MHz, respectively, at 37±0.2 °C. The accuracy of measurements of the ^{1}H chemical shifts was 0.01 ppm. IR spectra were recorded on a Specord 75IR instrument in the KBr pellets.

Results and Discussion

The ^{1}H NMR spectra of solutions of the PW_{12} and S_2Mo_{18} salts (see Table 1) exhibit a single peak for the hydroxyl protons of chloral hydrate molecules (see Fig. 1, peak *2*); the peak virtually coincides with that observed in the spectrum of the individual substance. This can be explained by the fact that chloral hydrate virtually does not react with low-basicity anions. In the spectra of the SiW_{12} and PMo_{12} salts, this signal slightly shifts downfield, pointing to a weak interaction, while in the case of PMo_{12}, it additionally splits into two components. The ^{31}P NMR spectra show that the composition and structure of the hetero polyanion are completely retained and no noticeable (on the δ ^{31}P NMR time scale) complexation is involved because the phosphorus atom shielded by the oxometallate shell is insensitive to weak outer-sphere interactions such as hydrogen bonds. The authors of earlier studies**[6,7]** presented no data on the splitting of the signal of the OH groups, apparently, due to the insufficient resolving power of the spectrometers used.

The splitting of the signal of the chloral hydrate OH groups can be due the difference between the structures of the molybdate and tungstate HPA anions or to the incorrectness of the initial assumption**[6]** that only O_b atoms are involved in complexation. The W and Mo Keggin anions have formally identical structures (see Fig. 1). However, semiempirical calculations (with the assumption of an ideal structure of the anions) showed**[10]** that the mean atom charges of the O_b and O_t atoms in the W-anions are identical (*i.e.*, the anion surface should be homogeneous in charge density), while in the case of Mo anions, the O_t atoms should have a lower charge than O_b. However, the Keggin W-anions are highly symmetrical (T_d), whereas Mo-anions have a lower symmetry, closer to the T group, due to the displacements of the Mo atoms inside the octahedra. The displacements result in alternation of shortened and elongated Mo—O_b—Mo bonds.**[11,12]** It can be concluded that the surface of the Keggin W-anions is more uniform regarding the acid-base properties than the surface of Mo-anions; this accounts for the fact that at least two types of complexes of PMo_{12} with chloral hydrate can be observed in the ^{1}H NMR spectrum.

The spectra of solutions of P_2Mo_{18} (see Table 1) exhibit one broadened signal due to the OH groups of chloral hydrate; in the spectra of P_2W_{18}, this signal is always split. The ^{31}P NMR spectra also did not show any changes in the structure or composition of the heteropoly anions. The Dawson anions consist of two structurally nonequivalent MO_6 octahedra of two types, those in belts (12 MO_6) and in polar caps (6 MO_6) (see Fig. 1). This corresponds to the presence of O_t atoms of two types and O_b atoms of five types discernible in the ^{17}O NMR spectra.**[13]** A simplified semiempirical calculation of the mean charges on the O atoms in the Dawson W- and Mo-anions**[14]** gave identical results for O_t and O_b. However, studies of the oxygen exchange in the anions**[13]** and the thermal stability of HPA**[15]** showed that all the O atoms in the polar caps are much more labile than those in the anion belts. As applied to the goals of the present work, this can be interpreted as the presence of two regions with different properties on the surface of the oxygen shell of the Dawson anions, at the belt and at the polar caps. Correspondingly, the spectra of solutions of salts of the symmetrical P_2W_{18} anion exhibit two signals corresponding to complexes of two types (see Table 1). In the case of P_2Mo_{18}, due to the specific properties of the MoO_6 octahedra,**[11,12]** the situation is complicated by even greater distortions of the anion than those observed in PMo_{12}. Apparently, the broad signal from the OH groups is a superposition of several signals caused by the interaction of chloral hydrate with a highly inhomogeneous oxygen shell of P_2Mo_{18}.

The spectra of solutions of salts of larger anions, P_2W_{21} and As_2W_{21}, (see Fig. 1) exhibit three signals with different intensities for the hydroxyl protons of chloral hydrate (see Table 1). This points to a complex (wavy) profile of the basic properties on the anion surface.

In the presence of a salt of the poorly studied B_3W_{39} HPA (the structure of the anion according to published data**[16]** is presented in Fig. 1), the ^{1}H NMR spectra exhibit three signals for the hydroxyl protons with approximately equal intensities. In view of the complexity of the ^{183}W NMR spectrum of an aqueous solution of the B_3W_{39} HPA, which consists of three packages of lines (data for B_3W_{39} will be published elsewhere), it can be concluded that the three BW_{13} structural units that constitute the B_3W_{39} anion are nonequivalent. The small number of replaceable (acidic) protons that we found (11 of 21, as confirmed by the potentiometric titration of a dioxane solution of the B_3W_{39} HPA) also point to a specific structure of this anion in solution compared to that in the crystalline state, in which the B_3W_{39} anion was reported**[16]** to be symmetrical.

The results indicate that the surface of many heteropoly anions is nonuniform in acid-base properties.

Due to splitting of the signals of the chloral hydrate hydroxyl protons in the ^{1}H NMR spectra of solutions of the HPA salts with various structures, this signal cannot be used to make a comparative estimate of the overall basicity of heteropoly anions, as has been done previously.**[6,7]** For this estimate, we used the relatively pronounced change in the position of the signals of the chloral hydrate CH protons (see Fig. 2, peak *1*). The data are presented in Fig. 3. The results obtained for HPA salts of the Keggin structure are closely similar to those obtained previously.**[7]** Since heteropoly anions of different structures differ substantially in size and are potentially capable of coordinating dissimilar numbers of chloral hydrate molecules, direct comparison of the data using Fig. 3 for these anions is illegitimate. The data presented in Fig. 4, which are the Δδ $^1H_{CH}$ values divided by the number of W or Mo atoms in the anion, are more illustrative. The ratio of the anion charge to the number of W or Mo atoms in the anion, *i.e.*, the mean specific charge (MSC) per W or Mo atom, can be taken as an additional parameter for comparison. In this respect (see Fig. 4), heteropoly anions can be divided into three groups: S_2Mo_{18}, PW_{12}, and PMo_{12} (MSC = 0.22—0.25); P_2W_{21}, SiW_{12}, As_2W_{21}, and B_3W_{39} (MSC = 0.28—0.33, taking the number of acidic protons in B_3W_{39} to be 11); and P_2Mo_{18} and P_2W_{18} (MSC = 0.33). Since a decrease in Δδ $^1H_{CH}$, as in Δδ $^1H_{OH}$, reflects lowering of the basicity, heteropoly anions can be arranged in terms of the basicity in the

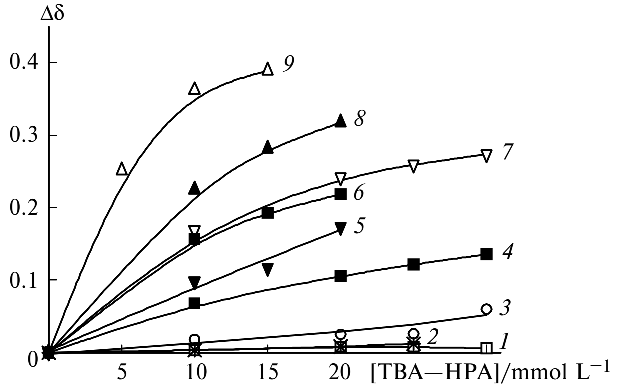

Fig. 3. Position of the ^{1}H NMR signal of the CH group of chloral hydrate *vs.* concentration of the HPA salt: PW_{12} (*1*), S_2Mo_{18} (*2*), PMo_{12} (*3*), SiW_{12} (*4*), P_2W_{21} (*5*), As_2W_{21} (*6*), P_2Mo_{18} (*7*), P_2W_{18} (*8*), B_3W_{39} (*9*).

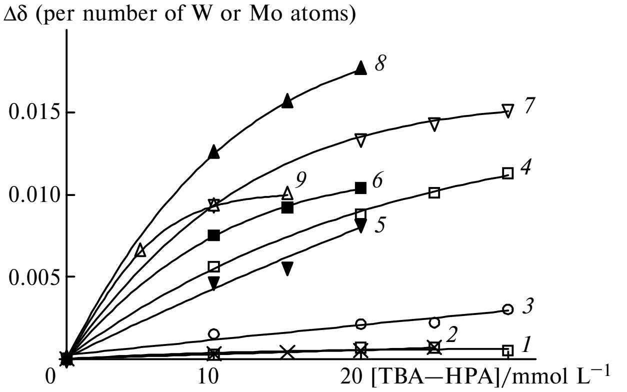

Fig. 4. Variations of δ $^1H_{CH}$ related to the number of the W or Mo atoms in the heteropoly anions. For designations, see Fig. 3.

following series: group 1 < group 2 < group 3. In the general case, the specific charge per W or Mo atom varies in the same order. Thus, although the surface of the HPA anions is inhomogeneous, the foregoing generally confirms the correlation found previously for the HPA anions of the Keggin structure,[7] namely, with a decrease in the anion charge, the anion basicity decreases and, hence, the acidity of the corresponding HPA increases. Apparently, some contribution to the Δδ ^{1}H values (see Fig. 3 and 4) is made by the residual protons present in the P_2W_{18}, P_2Mo_{18}, and P_2W_{21} salts. However, even if this factor does exist, it is not sufficiently strong to disrupt the general pattern.

Although the S_2Mo_{18} HPA in a pure state is unknown (we did not isolate it either), the results obtained demonstrate that this HPA should be a fairly strong acid, at least as strong as PW_{12}. The anions of strong acids such as PW_{12} and S_2Mo_{18} virtually do not react with chloral hydrate; hence, their basicity cannot be estimated in this way.

Thus, the ^{1}H NMR study of the complexation between chloral hydrate and heteropoly anions made it possible to conclude that the structure of HPA anions can exert a dual influence on the acidic and catalytic properties of HPA. First, the anion structure affects the overall acidity of the HPA, which can be compared with the MSC values. Second, the surface of the anion can be nonuniform in acid-base properties. When HPA or their salts are used in catalysis, the nonuniformity can create prerequisites for the most or least advantageous adsorption (activation) of organic molecules of various types on the surface of the HPA anion. As a consequence, the catalytic properties of HPA in both heterogeneous and homogeneous acidic-type liquid-phase reactions depend on both the overall acidity of the HPA and the type of the reactant.[4]

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