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Electronic Effects on the Enthalpy of Specific Interaction of Three-Coordinate Phosphorus Compounds and Acetals with Chloroform

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Abstract—The effect of electronic factors in five- and six-membered cyclic three-coordinate phosphorus compounds and acetals on the enthalpy of their specific interaction with chloroform was estimated.

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Calorimetric studies on series of structurally related organic and heteroelement-containing compounds can provide information on various factors, including electronic, that are responsible for their intermolecular interactions. In continuation of our thermochemical studies on organophosphorus compounds [1, 2], in the present work we examined by the calorimetric method dissolution of some series of three-coordinate phosphorus derivatives and their carbon analogs in hexane, carbon tetrachloride, and chloroform at 298 K. Chloroform was selected with a view to estimate the ability of the above compounds to form hydrogen bonds as hydrogen acceptors.

As a rule, molecules of organophosphorus compounds possess several centers capable of accepting a proton from proton donors: these are heteroatoms having lone electron pairs (P, O, N, S, and halogen atoms) and π-electron systems. Participation of one or another fragment in H-complex formation is determined, among other factors, by the nature of hydrogen donor. For example, phosphites are known to undergo protonation by the action of strong acids at the phosphorus atom (see [3] and references given therein). By contrast, phosphorus and chlorine atoms in dialkyl phosphites and chlorophosphines do not interact directly with such weak hydrogen donors as phenylacetylene [4] and chloroform [1]. Therefore, specific interactions of three-coordinated phosphorus compounds and acetals with chloroform (provided that the latter is present in a large excess) involve all possible centers and have similar origins; their enthalpy is contributed mainly by the enthalpies of paired donor–acceptor interactions of the hydrogen donor with lone electron pairs on the oxygen atoms.

We previously determined [1] the enthalpies of solvation of various three-coordinate phosphorus compounds and acetals. On the basis of these data and those obtained in the present work we calculated the average enthalpies of their specific interaction with chloroform, which are collected in Table 1. Benzaldehyde and acetaldehyde acetals (series **E** and **F**, respectively) are generally stronger electron donors than cyclic three-coordinate phosphorus compounds (series **A**–**C**). Among organophosphorus compounds, the enthalpy of specific interaction with chloroform decreases in going from five- to six-membered analogs, while phosphorus-free cyclic acetals display the reverse relation.

The observed variation in the basicity of heterocyclic compounds can be interpreted in terms of the anomeric effect [5, 6] related to n_O–σ^*_{X-Y} interactions (where X = CH, P; Y is an exocyclic group; n_O is *p* orbital bearing lone electron pair of an endocyclic heteroatom) between lone electron pairs on the endocyclic oxygen atoms and antibonding molecular orbital of the exocyclic bond. Obviously, this effect should be stronger in 1,3,2-dioxaphosphinanes, and it should weaken in going to five-membered cyclic phosphites {POC angle is ~118–120° (sp^2-orbital of the oxygen LEP) or ~111–112° (sp^3-orbital [7]), respectively}.

Table 1. Average enthalpies of specific interaction with chloroform (kJ/mol; 298 K) of five- and six-membered heterocyclic compounds [ORO]XR′ (**I**–**XXXVII**)

Comp. no.	R	X	R′	$-\Delta H_{sp}$	Comp. no.	R	X	R′	$-\Delta H_{sp}$
Series **A**									
I	$(CH_2)_2$	P	OMe	8.9±0.4	**IV**	$(CH_2)_3$	P	OBu	8.3±0.2
II	MeCHCHMe	P	OEt		**V**	$MeCH(CH_2)_2$	P	OMe	
III	Me_2CCMe_2	P	OEt		**VI**	$MeCH(CH_2)_2$	P	OEt	
					VII	$CH_2C(Me)_2CH_2$	P	OMe	
					VIII	$CH_2C(Me)_2CH_2$	P	OEt	
Series **B**									
IX	$MeCHCH_2$	P	$OSiMe_3$	6.9±0.1	**XI**	$MeCH(CH_2)_2$	P	$OSiMe_3$	5.7±0.3
X	MeCHCHMe	P	$OSiMe_3$		**XII**	$CH_2C(Me)_2CH_2$	P	$OSiMe_3$	
Series **C**									
XIII	$(CH_2)_2$	P	Cl	5.6±0.1	**XVII**	$(CH_2)_3$	P	Cl	4.7±0.3
XIV	$MeCHCH_2$	P	Cl		**XVIII**	$MeCH(CH_2)_2$	P	Cl	
XV	MeCHCHMe	P	Cl		**XIX**	$CH_2C(Me)_2CH_2$	P	Cl	
XVI	Me_2CCMe_2	P	Cl						
Series **D**									
–					**XX**	$CH_2C(Me)_2CH_2$	P	Ph[a]	10.2±0.5
Series **E**									
XXI	$(CH_2)_2$	CH	Ph[a]	9.7±0.5	**XXV**	$(CH_2)_3$	CH	Ph[a]	11.3±0.5
XXII	$MeCHCH_2$	CH	Ph[a]		**XXVI**	$CH_2C(Me)_2CH_2$	CH	Ph[a]	
XXIII	MeCHCHMe	CH	Ph[a]						
XXIV	Me_2CCMe_2	CH	Ph[a]						
Series **F**									
XXVII	$MeCHCH_2$	CH	Me	9.0±0.2	**XXX**	$MeCH(CH_2)_2$	CH	Me	9.8±0.3
XXVIII	MeCHCHMe	CH	Me		**XXXI**	$CH_2C(Me)_2CH_2$	CH	Me	
XXIX	Me_2CCMe_2	CH	Me						
Series **G**									
XXXII	$(CH_2)_2$	CH	$C_6H_4NO_2$-*p*	15.7±1.4	**XXXVI**	$(CH_2)_3$	CH	$C_6H_4NO_2$-*p*	14.6±0.1
XXXIII	$(CH_2)_2$	CH	$C_6H_4NO_2$-*m*		**XXXVII**	$(CH_2)_3$	CH	$C_6H_4NO_2$-*m*	
XXXIV	MeCHCHMe	CH	$C_6H_4NO_2$-*p*						
XXXV	Me_2CCMe_2	CH	$C_6H_4NO_2$-*p*						

[a] The contribution of phenyl group to the enthalpy of specific interaction was estimated at –1.4±0.1 kJ/mol on the basis of the data for dissolution of triphenylmethane and triphenylphosphine.

Here, the larger the contribution of the oxygen LEPs to intramolecular interactions, the lower their ability to act as proton acceptors, as we observed for series **A**–**C** compounds.

Analogous effects are almost absent in acetals (series **E** and **F**) [6] due to high energy of σ^*_{C-R} orbitals. Presumably, the same factor is responsible for the absence of anomeric effect in organophosphorus compounds having exocyclic P–R bond [6], which was found previously by analysis of the electron density distribution in phenylphosphonites and triphenylphosphine where *n*–π orbital mixing is very weak [8]. One

Table 2. Enthalpies (kJ/mol, 298 K) of dissolution (ΔH_{dis}), solvation (ΔH_{solv}), specific interaction with chloroform (ΔH_{sp}), and vaporization (ΔH_{vap}) and molecular refractions of cyclic *p*- and *m*-nitrobenzaldehyde acetals **XXXII–XXXVII** and nitrobenzene (**XXXVIII**)

Comp no.	C_6H_{14}		CCl_4			$CHCl_3$			MR_D	ΔH_{vap}
	ΔH_{dis}	ΔH_{solv}	ΔH_{dis}	ΔH_{solv}		ΔH_{dis}	ΔH_{solv}	ΔH_{sp}		
				found	calculated[a]					
XXXII	37.7	–51.7	30.1	–59.3	–59.0	15.8	–73.6	–14.3	46.7	89.4
XXXIII	41.0	–51.7	32.6	–60.1	–59.0	16.3	–76.4	–16.3	46.7	92.7
XXXIV	37.7	–56.8	27.2	–67.3	–63.9	11.3	–83.2	–15.9	54.7	94.5
XXXV	33.9	–60.0	24.3	–69.6	–67.1	8.0	–85.9	–16.3	64.2	93.9
XXXVI	34.7	–56.7	28.4	–63.0	–63.8	13.8	–77.6	–14.6	51.4	91.4
XXXVII	33.9	–56.7	25.5	–65.1	–63.8	10.9	–79.7	–14.6	51.4	90.6
XXXVIII	–	–39.0[b]	4.2[c]	–46.8[d]	–46.7	–2.5	–53.5	–6.7	33.0	51.0[e]

[a] Calculated by the equation $-\Delta H_{\text{solv}}(CCl_4) = 13.0 + 1.02MR_D$ [10].

[b] Calculated by the equation $-\Delta H_{\text{solv}}(C_6H_{14}) = 4.39 + 1.05MR_D$ [1].

[c] Calculated by the equation $\Delta H_{\text{dis}} = \Delta H_{\text{vap}} + \Delta H_{\text{solv}}$ [1].

[d] Data of [11].

[e] Data of [12].

more support for the above stated may be similar P–Ph bond lengths in the molecules of triphenylphosphine and 4-methyl-6-methylidene-2-phenyl-6*H*-1,3,2-dioxaphosphinine (1.828, and 1.826 Å, respectively [6]). The enthalpies of specific interaction with chloroform of 4,5-dimethyl-2-phenyl-1,3,2-dioxaphosphinane and its carbon analog, 4,5-dimethyl-2-phenyl-1,3-dioxane, were estimated at –10.2 and –10.9 kJ/mol, respectively. The corresponding value for, e.g., 2-chloro-4,5-dimethyl-1,3,2-dioxaphosphinane is considerably lower, –4.4 kJ/mol. Provided that anomeric effect is absent, the basicity of lone electron pairs on oxygen atoms is determined only by their hybridization; therefore, 1,3-dioxanes are more basic than their five-membered analogs.

The energy of $\sigma^*_{\text{C–R}}$ orbitals in cyclic acetals can be reduced via introduction of an electron-withdrawing group into the exocyclic substituent R (Table 1). Decrease in the energy difference between the n_{O} and $\sigma^*_{\text{C–R}}$ levels should favor their more effective interaction. This was observed by us previously while studying the IR spectra and polarographic behavior of acetals derived from *p*- and *m*-nitrobenzaldehydes [9]. Therefore, the basicity series in group **G** compounds (Table 1) should be reversed with respect to that in series **E** and **F** and should be similar to series **A–D**. To verify this assumption we determined the enthalpies of specific interaction of acetals **XXXII–XXXVII** with chloroform (Table 2).

The average enthalpies of specific interaction of nitrobenzaldehyde acetals with chloroform are given in Table 1. In fact, this parameter somewhat increases in going from six-membered (**XXXVI** and **XXXVII**) to five-membered cyclic derivatives (**XXXII–XXXV**), as in the phosphite series. The contribution of the interaction of the $C_6H_4NO_2$ group with chloroform to the overall ΔH_{sp} values of compounds **XXXII–XXXVII** can be estimated on the basis of the enthalpy of specific solvation of nitrobenzene (**XXXVIII**) by chloroform, which was calculated from our experimental and published data (–6.7 kJ/mol, Table 2).

Although our results support the above concepts on the effect of electronic factors on the ability of five- and six-membered cyclic compounds to form hydrogen bonds with chloroform, these effects produce only slight variation of the enthalpy of specific interaction, so that we can note only an appreciable tendency.

EXPERIMENTAL

Organophosphorus compounds **I–XXXI** were synthesized and purified as described in [1]. Nitrobenzaldehyde acetals **XXXII–XXXVII** were synthesized according to the procedure reported in [9], and their physical constants were in agreement with published data. Nitrobenzene (**XXXVIII**) and solvents were purified and dehydrated by standard methods [13]. The procedure for calorimetric measurements was described in [1, 2].

The enthalpies of vaporization of nitrobenzaldehyde acetals **XXXII–XXXVII** were calculated using Solomonov's equation [14, 15] from the experimental enthalpies of dissolution in hexane and molecular refractions. The total enthalpies of solvation were calculated from the dissolution and vaporization parameters. The enthalpies of specific interaction with chloroform were calculated from the differences in the enthalpies of solvation in chloroform and carbon tetrachloride [1].

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