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Vapour-phase Infrared Spectra of Ethyl Derivatives of Zinc, Cadmium and Mercury

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Vapour-phase vibration spectral data of molecules are necessary for the investigation of intermolecular interactions. On these bases the influence of molecular environment may be minimized and thus we can eliminate distortion of molecular normal vibration modes. There are some data in the literature on vibration spectra of compounds of type R_2M (M = Zn, Cd, Hg; R = CH_3, C_2H_5) in liquid state and in solution [1–4]. In one paper [4] there are some solid state and vapour-state spectra of methyl derivatives of zinc, cadmium and mercury as well as liquid state spectra.

We were interested in getting the vapour-state infra-red spectra of di-ethyl compounds of Zn, Cd and Hg.

Experimental

Ethyl derivatives of Group IIB metals have been obtained following the literature data: Et_2Zn [5], Et_2Cd [6] and Et_2Hg [7, 8].

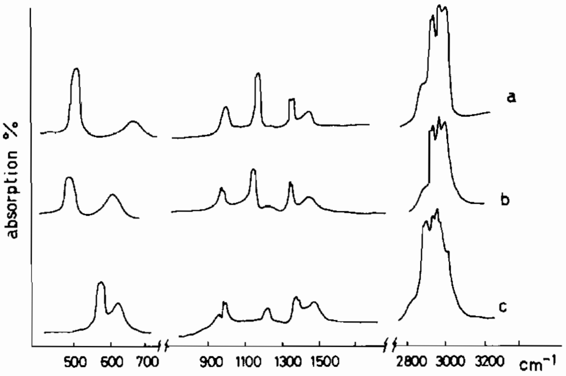

Fig. 1. Infrared spectra of ethyl derivatives: a) Hg, b) Cd, c) Zn.

IR spectra were registered in a cell [9], from which the mirror table had been removed, on a Carl Zeiss spectrophotometer UR-20 in the range 400–4000 cm^{-1}. Spectral slit width in the range 1000 cm^{-1} was 4 cm^{-1}.

The spectrum of Et_2Zn was registered at 25 °C, vapour pressure of Et_2Zn was 20 torr, Et_2Cd at 53 °C and 16 torr, Et_2Hg at 75 °C and 28 torr [8]. The spectra are represented in Fig. 1.

Results and Discussion

The most interesting absorption bands are located in the range 400–1700 cm^{-1} (see Table I). Only the antisymmetrical (ν_3) stretching mode is active in the infrared vibration spectrum of symmetrical linear three-mass molecule R_2M (point group is $D_{\infty h}$). Symmetrical (ν_1) stretching mode is active in Raman spectrum according to selection rules; δ deformation mode is located below 400 cm^{-1}. Distortion of linear molecule configuration leads to a point group

TABLE I. Infrared Spectra of Et_2Zn, Et_2Cd, Et_2Hg in Vapour Phase.

No	Et_2Zn	Et_2Cd	Et_2Hg	Assignment [3]
1	569	500	517	Q ν_{as} (C–M–C)
2	615	617	667	ρ(M–CH_2)
3	948	951	951	ρ(C–CH_3)
4	959	961		ρ(C–CH_3)
5	985	993	1015	ρ(C–CH_3)
6	993	1003	1022	ρ(C–CH_3)
7	1180	1153	1193	ρ(C–CH_3)
8	1215	1235	1235	ω_α(CH_2)
9	1375	1375	1375	$\delta_{s\alpha}$(CH_3)
10	1383	1383	1385	$\delta_{s\alpha}$(CH_3)
11	1479	1458	1458	$\delta_{as\alpha}$(CH_3)

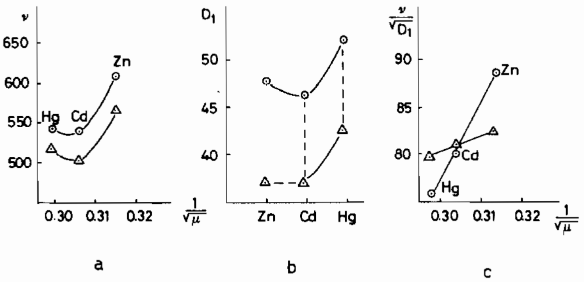

Fig. 2. Influence of reduced mass and metal–carbon bond strength upon antisymmetrical stretching mode of this bond in zinc, cadmium and mercury alkyls; a) no correction on dissociation energy D_1; b) D_1 values for zinc, cadmium and mercury alkyls; c) with correction on D_1. ○ methyl, △ ethyl.

C_{2v} (in a case of conservation of radical equivalency) and to removal of prohibition and both stretching modes become active in the infra-red spectrum [10]. Intermolecular interaction in liquid phase leads to small deviations from linear configuration of such molecules as R_2M. This is confirmed by the existence of weak absorption bands in liquid phase spectra of ethyl derivatives of zinc (480 cm^{-1}) and cadmium (440 cm^{-1}), assigned to ν_1 [3].

Intermolecular interactions in vapour phase are practically absent, and there were not found the absorption bands corresponding to symmetrical stretching mode ν_1 in infra-red spectra of diethylzinc, diethylcadmium and diethylmercury. That is, molecules of ethyl derivatives of Zn, Cd and Hg have the greatest extent of linear configuration as was expected. Perhaps the decrease of intermolecular interaction effect in vapour phase leads also to a decrease of absorption band widening assigned to $C–CH_3$ rocking modes (see Table I). Antisymmetrical stretching ν_3 (C–M–C) modes in methyl derivatives of metals considered decrease in the series: Zn > Hg > Cd, and differences $\nu_{Zn} - \nu_{Cd} = 70\ cm^{-1}$ and $\nu_{Hg} - \nu_{Cd} = 10\ cm^{-1}$ [4]. A similar trend is observed also in a series of ethyl derivatives, and $\nu_{Zn} - \nu_{Cd} = 70\ cm^{-1}$, $\nu_{Hg} - \nu_{Cd} = 20\ cm^{-1}$ (in vapour), $\nu_{Hg} - \nu_{Cd} = 40\ cm^{-1}$ (in liquid).

As was mentioned in [4] the spectral difference of R_2Hg, where R = CH_3, C_2H_5, is due to the greater strength of the Hg–C bond. To check it we have plotted against $1/\sqrt{\mu}$, where μ is the reduced mass of C–M oscillator (Fig. 2a). On the basis of this we can conclude that wavenumber differences of metal–carbon bond stretching modes are certainly determined by C–M bond strength [11] as well as by metal atom mass effect. This is confirmed by a linear dependence of ν_3 on $1/\sqrt{\mu}$ with allowance for bond dissociation energy D_1 [12, 13] for methyl derivatives. As follows from a general consideration, antisymmetrical ν_3 stretching mode must correlate with dissociation energy of the first radical D_1:

$$\text{R–M–R} \xrightarrow{D_1} \text{R–M} + \text{R}$$

$$\underset{\rightarrow\ \leftarrow\ \rightarrow}{\text{R–M–R}}\ (\nu_3)$$

There is no D_1 value for Et_2Cd in the literature, and we have found the unknown D_1 value by interpolation (see Fig. 2b). The suggestion about a linear dependence of ν_3 for ethyl derivatives of Zn, Cd, Hg on $1/\sqrt{\mu}$ with allowance for D_1 as well as for methyl derivatives leads to the same dissociation bond D_1 (Et–CdEt) energy.

Conclusion

1. Vapour-phase infrared spectra of diethylzinc, diethylcadmium and diethylmercury were obtained in the range 400–4000 cm^{-1}.

2. These spectra correspond to a linear structure of Et_2M (M = Zn, Cd, Hg) molecules in the vapour phase.

3. The dependence of wavenumbers of antisymmetrical stretching vibration modes for methyl and ethyl derivatives of zinc, cadmium and mercury on reduced C–M oscillator mass and the first dissociation energy D_1 was shown.

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