The Heats of Adsorption of Some Chlorinated Hydrocarbons on Porous γ-Alumina

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The limiting isosteric heats of adsorption on γ-alumina were determined by gas-solid chromatography in the temperature range 150—225 °C for the compounds: CCl_4 (9.0 kcal/mol), $CHCl_3$ (10.2), CH_2Cl_2 (9.9), $CH_3—CCl_3$ (8.2), $CH_2Cl—CHCl_2$ (8.2 and 9.6 according to adsorption position). The results are discussed with regard to possible orientations of the adsorbed molecules on the solid surface as well as to the interaction of the electric surface field with the adsorbate molecular dipoles.

Gas chromatographic procedures find increasing interest for evaluating thermodynamic quantities relevant to physical adsorption [1] and have been used in this laboratory for determining the heats of adsorption of several hydrocarbons on solid adsorbents [2, 3]. It was shown that with linear alifatic compounds the adsorbate-adsorbent interactions are non-specific in nature and largely due to dispersion forces, whereas unsaturated or aromatic compounds clearly showed a contribution from the electrostatic interaction with the adsorbate π-electron system.

It was thought worth extending the research to other organic vapours which, contrary to the apolar ones studied previously, have a permanent electric moment. In the present work the heats of adsorption for $CHCl_3$, CH_2Cl_2, $CH_3—CCl_3$, $CH_2Cl—CHCl_2$ (and CCl_4 for comparison) on γ-Al_2O_3 were determined, aiming at revealing the interaction of the surface electric field with the adsorbate molecular dipoles and possibly obtaining information on the orientation of the adsorbed molecules on the surface.

Experimental

Materials. B.D.H. γ-Al_2O_3 "for chromatographic adsorption analysis", from the same batch used previously (BET nitrogen area $= 148 \pm 2$ m²/g) was activated at 300 °C in air before column packing and then flushed with the carrier gas for 6 hrs. at 200 °C.

As for the adsorbates, Merck "Uvasol" $CHCl_3$ and CH_2Cl_2 and C.Erba "RS" CCl_4 and $CH_3—CCl_3$ were employed without further purification; Fluka

"Purum" (98%) $CH_2Cl—CHCl_2$ was purified by known methods [4-6] and repeatedly distilled ($n_D^{20} =$ 1.47146; lit.: $n_D^{20} = 1.4715$ [6]). A purity check, required after the experimental observations referred to below, was made by GLC (stationary phase: Apiezon Grease L on 60 – 80 mesh Celite) and gave $>99.7\%$.

Apparatus and procedure. The experimental set-up for measuring gas chromatographic retention times, column temperatures and carrier gas flow-rates was essentially the same as described previously [2]. True retention times [7] at several temperatures were measured with constant flow-rates (throughout each experimental run) for injected samples of 0.1 to 2 μl (i. e., about 1 to 30 μmol) and corrected for the temperature difference between column and flow-meter and for the pressure drop across the column, according to James and Martin [8].

Two independent runs were always made with each adsorbate.

Electrolytic hydrogen (99.995%) was employed in all cases but for one run with $CH_2Cl—CHCl_2$ where helium (99.9%) was used.

The experimental conditions are summarized in Table 1.

Results. Plotting $\log t$ vs. $1/T$ ($t =$ corrected retention time, $T =$ abs. temperature) for each injected amount, straight-lines were always found. By least squares fitting of data to the equation $\log t = a + b/T$, the heat of adsorption, Q_a, was gained from the slope $b = Q_a/2.303\, R$. The results are reported in Table 2.

It should be noted that two sets of data are reported for $CH_2Cl—CHCl_2$: this derives from an unexpected feature in the chromatograms of this compound, which always exhibited two distinct

Column: stainless steel; length 100 cm; i. d. 0.6 cm					
Adsorbate	Run	Carrier gas	Temperature range [°C]	Flow rate [ml/min]	Pressure drop range [atm]
CCl_4	1	H_2	160 − 202	100	0.92 − 1.02
	2	H_2	155 − 196	100	0.90 − 1.00
$CHCl_3$	1	H_2	160 − 200	100	0.91 − 1.02
	2	H_2	160 − 200	100	0.91 − 1.01
CH_2Cl_2	1	H_2	150 − 190	105	0.92 − 1.03
	2	H_2	150 − 190	105	0.92 − 1.03
$CH_3 - CCl_3$	1	H_2	165 − 200	60	0.62 − 0.68
	2	H_2	165 − 200	60	0.62 − 0.68
$CH_2Cl - CHCl_2$	1	H_2	200 − 225	100	1.02 − 1.08
	2	He	195 − 225	75	1.19 − 1.26

Table 2. Heats of adsorption, Q_a (kcal/mol), measured for different injected sample amounts (μmol).

CCl_4	μmol	1.03	3.09	5.15	7.21	10.30	20.59
	Q_a	8.92	8.84	8.79	8.74	8.72	8.67
$CHCl_3$	μmol	1.24	3.72	6.20	8.68	12.40	24.79
	Q_a	10.14	9.75	9.79	9.71	9.76	9.63
CH_2Cl_2	μmol	1.60	4.81	8.02	11.23	16.04	32.07
	Q_a	9.70	9.62	9.50	9.37	9.29	9.21
$CH_3 - CCl_3$	μmol	0.99	2.97	4.95	6.93	9.90	19.80
	Q_a	8.04	8.07	8.16	8.16	8.32	8.51
$CH_2Cl - CHCl_2$ (a)	μmol	1.08	3.24	5.40	7.56	10.79	21.58
	Q_a	8.08	8.07	7.89	7.91	7.79	8.04
$CH_2Cl - CHCl_2$ (b)	μmol	3.24	5.40	7.56	10.79	21.58	
	Q_a	9.55	9.44	9.47	9.48	9.53	

The standard deviation of Q_a[2,9] was usually $\pm 0.2 - 0.3$ and never exceeded 0.5 kcal/mol.

peaks. Since sample impurity was excluded, the occurrence of a chemical reaction in the adsorbed phase was suspected. This, however, could also be ruled out since: 1) no change occurred when helium was substituted to hydrogen as the carrier gas, and 2) very good base-line stability and peak reproducibility were always obtained. The fact might then be explained if the $CH_2Cl - CHCl_2$ molecules were adsorbed in two different positions with substantially differing values of the adsorption heat: would this be the case, the elution should take place at different rates originating two well resolved peaks. The data in Table 2 under the headings (a) and (b) refer to the peaks with shorter and longer retention times, respectively.

When the Q_a's obtained in one run were plotted vs. the adsorbate amount (which is proportional to surface coverage) a slight dependence on the coverage was observed: Figure 1 shows that extrapolation to zero coverage could be performed safely.

Very good agreement was found between the extrapolated values, $Q_{a,0}$, of different runs for each adsorbate: these values, together with the averages, are reported in Table 3.
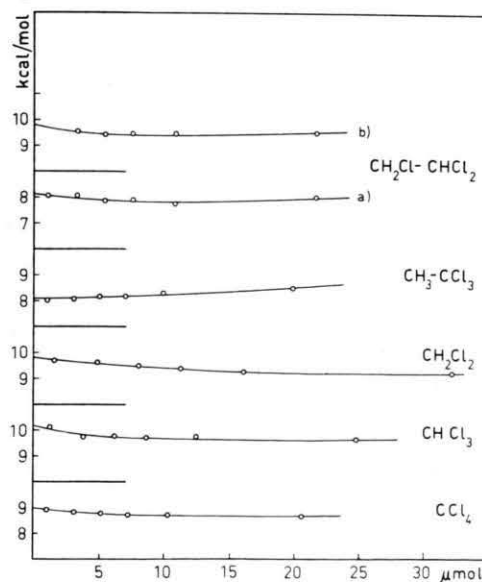

Fig. 1. Change of the chromatographic heat of adsorption with injected sample amount (data from runs 2).

Table 3. Chromatographic heats of adsorption (kcal/mol) at zero surface coverage.

Adsorbate	Run	$Q_{a,o}$	$\overline{Q}_{a,o}$
CCl_4	1	9.0	9.0
	2	9.0	
$CHCl_3$	1	10.1	10.2
	2	10.2	
CH_2Cl_2	1	10.0	9.9
	2	9.8	
CH_3-CCl_3	1	8.2	8.2
	2	8.1	
$CH_2Cl-CHCl_2$ (a)	1	8.2	8.2
	2	8.2	
$CH_2Cl-CHCl_2$ (b)	1	9.6	9.7
	2	9.8	

Discussion

As already stated [10] the gas chromatographic heat of adsorption at zero coverage coincides with the limiting isosteric heat; thus, it can be related directly to the adsorption potential [10, 11].

For $CHCl_3$, $Q_{a,0}$ is distinctly larger than for CCl_4. On the contrary, earlier measurements by Ross et al. [12] on graphitized carbon black gave almost equal values for the limiting isosteric heats of both adsorbates (8.00 and 8.35 kcal/mol, respectively). This different behaviour can be related to the stronger surface electric field of the oxidic adsorbent. While with CCl_4 the largest part of the adsorption potential can be attributed to the dispersion interaction, with the permanent dipole moment of $CHCl_3$ a significant contribution by electrostatic interaction is also to be expected. Further, in the case of a symmetrical molecule such as CCl_4 the question of the adsorption position does not arise, whereas with molecules of lower symmetry a position corresponding to a maximum of the dispersion interaction energy is favoured [13]; when the adsorbate has a permanent dipole moment further restriction to molecular rotation in the adsorbed layer results from the orienting effect of the surface field, which tends to align the dipoles parallel to the field and pointing to the surface. In the case of $CHCl_3$ both effects cooperate to favour the same orientation, since the moment (1.05 D [14]) lies on the symmetry axis and points to the Cl atoms plane.

Should the electrostatic energy, ε_e, of a polar molecule in an electric field be given [15] by $\varepsilon_e = -\mu F \cos \vartheta$ (where μ = dipole moment, F = electric field intensity at the centre of the dipole, ϑ = angle

between dipole and field directions), the energy is at a maximum when $\vartheta = 180°$. Thus, the $CHCl_3$ molecules should be adsorbed with their three chlorine atoms facing the surface. Incidentally, it may be remembered that the same orientation was demonstrated on different experimental grounds for $CHCl_3$ adsorbed on graphite [16].

Reported estimates of the surface field were in the order of $1-2 \times 10^5$ esu for alkali halides [17] and 2.7×10^5 esu for rutile [18]. With the rounded value of 10^5, the above equation gives for $CHCl_3$ $\varepsilon_e = 1.05 \times 10^{-20}$ J/molecule or $E_e = 1.5$ kcal/mol, which is close to the experimental difference in $Q_{a,0}$.

In CH_2Cl_2 the electric moment (1.57 D) is directed along the bisectrix of the $Cl-C-Cl$ angle. The orienting effect of the field should cause the molecules to be adsorbed in an "upright" position with the Cl atoms only contacting the surface. For the principle of maximum dispersion interaction, however, an "inclined" position with one H and two Cl atoms close to the surface should be preferred. It is readily seen from scale models that in the latter position it would be $\vartheta \approx 100°$, the electrostatic contribution thus becoming very small. Since an only slight lowering in the adsorption heat of CH_2Cl_2 with respect to $CHCl_3$ was found experimentally, it seems likely that an average adsorption position, closer to the "upright" one, is experienced by CH_2Cl_2.

With CH_3-CCl_3, $Q_{a,0}$ is significantly lower with respect not only to $CHCl_3$ but also to CCl_4. Since $\mu = 1.9$ D, an "upright" position analogous to that of $CHCl_3$ can be excluded, whereas a "lying-down" position with two Cl and two H atoms contacting the surface seems acceptable. On account of known bond polarizabilities, it may be guessed that even the dispersion energy term should be smaller than in the case of CCl_4; moreover, in this position $\vartheta \approx 90°$, the electrostatic term decreasing to a negligible value.

The case of $CH_2Cl-CHCl_2$ is more complicated by the possible existence of internal rotation isomers, while two distinct adsorption positions were experimentally detected. The value of the molecular dipole moment (1.4 D), as derived from gas-phase or dilute solution measurements, is of little aid here. Vector calculation from the individual $-CH_2Cl$ and $-CHCl_2$ group moments [19] gave 3.0 D and 0.6 D for the moments of the cis (staggered) and trans (eclipsed) configuration, respec-

tively. None of the measured adsorption heats seems able to correspond to adsorption of molecules in the *cis* configuration, on account of the high values both of the dipole moment and of the dispersion energy. With the *trans* configuration, mainly two types of adsorbed molecules can be considered (since any other possibility would not give a sufficiently high interaction energy): (i) with two H's and two Cl's, and (ii) with two Cl's and one H (pertaining to the same C atom), close to the surface. Stating the proper correspondence to these types of the two $Q_{a,0}$ values found is difficult. If, however, importance can be attached to the fact that with type (ii) the resultant moment (with $\vartheta \approx 150°$) would give an additional, even if moderate, energy contribution, the lower and higher values of $Q_{a,0}$ might be tentatively attributed to adsorbed $CH_2Cl - CHCl_2$ molecules of type (i) and (ii) respectively.

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[7] The actual elution time measured to maximum peak height was first corrected for the time required by a vapour to cover the distance from injection port to detector, at the given experimental conditions, in absence of adsorption. This was determined in each case by injecting $5-10 \mu$l of nitrogen.

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[19] In a first approximation these were taken as the moments for CH_3Cl (1.85 D) and CH_2Cl_2 (1.57 D) respectively.