man auch das absolute Minimum von U in dem durch die Schranken abgesteckten Raum findet, in einem ersten Durchgang alle Parameter mit einer relativ großen Schrittweite von der unteren bis zur oberen Schranke durchvariieren und erst dann, ausgehend von dem günstigsten Parametersatz, das beschriebene Sprungverfahren anschließen.

Unser Dank gilt der Deutschen Forschungsgemeinschaft, Bad Godesberg, und dem Fonds der Chemischen Industrie, Frankfurt a. M., für die finanzielle Förderung dieser Arbeit. Dem Leiter des Rechenzentrums der Universität des Saarlandes, Herrn Prof. Dr.-Ing. J. Dörr, danken wir für die Überlassung von Rechenzeit auf der Electrologica X 1.

Gas-solid Interaction

IV. Energy of Adsorption and Specific Interactions of Some Unsaturated and Cyclic Hydrocarbons on γ-Aluminium Oxide [○, *]

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(Z. Naturforsch. **25 a**, 688—692 [1970]; received 11 February 1970)

The heats of adsorption on weakly activated γ-Al_2O_3 of a number of linear 1-monoolefins (C_4 to C_9) and cyclic saturated and unsaturated hydrocarbons have been measured by gas-solid chromatography and extrapolated to zero surface coverage.

The double bond contribution to the adsorption energy is shown by comparison of the adsorption heats with those of the corresponding saturated molecules and is related to the existence of Brønsted acid centers on the adsorbent surface. The effect of cyclization is also shown.

In a previous paper [1], dealing with the energy of adsorption on γ-alumina of some saturated linear chain hydrocarbons, it was shown that gas-solid interactions in these systems are essentially dependent on dispersion forces only, which are known to be of a non-specific nature [2]. On the contrary, with systems "unsaturated molecule-oxidic surface" the conditions exist for specific interactions between particular functional groups (e. g., π-electron systems) and certain active centers of the surface [3]. The effects of such interactions (as due to electrostatic forces, hydrogen bond formation, etc.) have been already observed for the systems "silica gel – unsaturated hydrocarbons", both in the form of increments of the adsorption heats, and in the form of increased perturbation of the IR spectra of surface hydroxyls, as compared to those occurring in the adsorption of the corresponding saturated hydrocarbons on the same solid [4–8].

We were interested therefore in verifying experimentally the occurrence of specific interactions in the adsorption of unsaturated hydrocarbons on γ-Al_2O_3. Further, we have thought it interesting to search for a possible dependance of this effect on molecular size and on the degree of unsaturation within a given molecular pattern. For this purpose, the heats of adsorption, determined by the same gas-chromatographic method already employed [1], have been reported in this paper for six linear 1-alkenes (from C_1 to C_9), for the cyclic series cyclo-

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[○] Preceding papers: Z. Naturforsch. **22 a**, 203, 355 [1967]; **23 a**, 979 [1968].

[*] Work performed with the partial aid of Consiglio Nazionale delle Ricerche, Rome.

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hexane, cyclo-hexene, 1.4-cyclo-hexadiene and benzene, and finally for a cyclo-alkane series, including the terms from cyclo-pentane to cyclo-octane besides methyl-cyclopentane and methyl-cyclohexane.

Experimental

Materials. All of the adsorbates, except two, were Fluka products and were employed without further purification. Benzene and cyclohexane were C. Erba products of RS grade; these were repeatedly distilled from sodium wire before the measurements.

The adsorbent (from the same B.D.H. batch of γ-Al_2O_3 "for chromatographic analysis", employed in the preceding works) has been conditioned by heating at 300 °C in air for 24 hours and subsequent cooling down in a dessicator, before column packing. Before each series of gas-chromatographic runs the packed columns were flushed with the carrier gas (hydrogen) at 150 °C for 8 hours.

Adsorbate	Temperature range [°C]	Flow rate [ml/min]	Pressure drop range [atm]
1-butene	110—160	50	0.26—0.33
1-pentene	150—190	50	0.31—0.38
1-hexene	140—190	100	0.60—0.69
1-heptene	170—220	140	0.85—0.96
1-octene	180—230	140	0.87—0.98
1-nonene	190—230	140	0.93—0.98
cyclo-hexane	130—190	75	0.45—0.56
cyclo-hexene	150—200	75	0.47—0.56
1.4-cyclohexadiene	170—220	100	0.63—0.75
benzene	150—200	100	0.61—0.70
cyclo-pentane	110—160	75	0.42—0.49
methyl-cyclopentane	130—180	75	0.46—0.54
methyl-cyclohexane	140—190	100	0.60—0.70
cyclo-heptane	150—200	140	0.80—0.92
cyclo-octane	180—230	140	0.87—1.00

Table 1. Gas-chromatographic conditions.
Carrier gas: hydrogen.
Column: stainless steel, length 1 m, i. d. 0.6 cm.

Apparatus and procedure. For the determination of retention times in GSC, the same apparatus and procedure have been employed as in the previous work [1]. The experimental conditions are summarized in Table 1.

Results. From the slopes of the straight-line plots $\log t$ vs. $1/T$ (only a few examples of which are reported in Fig. 1) the heats of adsorption, Q_a, and the corresponding standard deviation, S_Q, were calculated by the procedure previously described [1, 9]. Both quantities are reported in Table 2, as a function of the injected sample amount: the Q_a values are also plotted in Fig. 2. These latter plots allow extrapolation to zero coverage, giving the values of Table 3.

1-butene	μmole	1.32	2.64	5.28	15.83		
	Q_a	8.48	8.43	8.35	8.35		
	S_Q	0.13	0.12	0.12	0.12		
1-pentene	μmole	0.92	4.61	6.45	9.21		
	Q_a	9.05	8.79	8.79	8.74		
	S_Q	0.08	0.11	0.15	0.10		
1-hexene	μmole	0.80	2.40	4.00	5.60	8.00	40.00
	Q_a	10.38	10.28	10.11	10.09	9.98	9.72
	S_Q	0.19	0.15	0.10	0.05	0.11	0.10
1-heptene	μmole	0.72	2.17	3.62	5.07	7.24	36.20
	Q_a	10.58	10.61	10.50	10.56	10.33	10.01
	S_Q	0.10	0.12	0.09	0.16	0.11	0.09
1-octene	μmole	1.91	3.19	4.46	6.38	31.90	
	Q_a	11.67	11.60	11.47	11.34	10.81	
	S_Q	0.18	0.14	0.12	0.12	0.13	
1-nonene	μ-mole	2.93	4.10	5.86	29.30		
	Q_a	12.95	12.63	12.61	12.16		
	S_Q	0.28	0.26	0.24	0.28		
cyclo-pentane	μmole	1.06	3.19	5.31	7.43	10.62	53.10
	Q_a	7.82	7.58	7.57	7.54	7.48	7.45
	S_Q	0.25	0.18	0.17	0.16	0.16	0.14
cyclo-hexane	μmole	0.93	2.78	4.63	6.48	9.25	46.25
	Q_a	8.54	8.38	8.30	8.27	8.18	8.07
	S_Q	0.15	0.14	0.12	0.12	0.10	0.09
cyclo-heptane	μmole	0.84	2.53	4.21	5.89	8.42	42.10
	Q_a	9.45	9.17	9.08	9.09	9.01	8.75
	S_Q	0.08	0.06	0.11	0.05	0.08	0.08
cyclo-octane	μmole	0.76	2.27	3.79	5.30	7.57	37.85
	Q_a	10.52	10.36	10.20	10.06	9.82	9.68
	S_Q	0.09	0.04	0.06	0.08	0.07	0.04
methyl-cyclo-pentane	μmole	0.89	2.67	4.45	6.22	8.89	44.45
	Q_a	8.92	8.64	8.58	8.47	8.72	8.09
	S_Q	0.26	0.23	0.19	0.19	0.34	0.31
methyl-cyclo-hexane	μmole	0.80	4.00	7.99	39.95	79.90	
	Q_a	9.58	9.43	9.29	8.99	8.92	
	S_Q	0.16	0.15	0.14	0.15	0.08	
cyclo-hexene	μmole	0.99	2.96	4.94	6.91	9.87	49.35
	Q_a	9.90	9.81	9.68	9.58	9.56	9.20
	S_Q	0.16	0.15	0.16	0.14	0.15	0.10
1.4-cyclo-hexadiene	μmole	1.06	3.17	5.29	7.40	10.57	52.85
	Q_a	10.98	10.86	10.75	10.67	10.50	10.23
	S_Q	0.28	0.27	0.22	0.19	0.23	0.16
benzene	μmole	1.13	3.38	5.63	7.88	11.25	56.25
	Q_a	10.49	10.43	10.31	10.15	10.23	9.87
	S_Q	0.23	0.15	0.15	0.15	0.14	0.12

Table 2. Heats of adsorption, Q_a, and standard deviations, S_Q, (both in kcal/mole), measured for different injected amounts (μmole).

Discussion

Surface Active Centers and Specific Interactions

The surface of refractory oxides, such as Al_2O_3, exposed to moist air is normally covered, in part or completely, by a layer of chemisorbed water [10] mainly in the form of hydroxyls [11]. Other surface

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[9] See Ref. [1], note 7.

[10] A. G. OBLAB, S. W. WELLER, and G. A. MILLS, Proc. 2nd Int. Congr. Surface Activity, op. cit. [3], p. 309.

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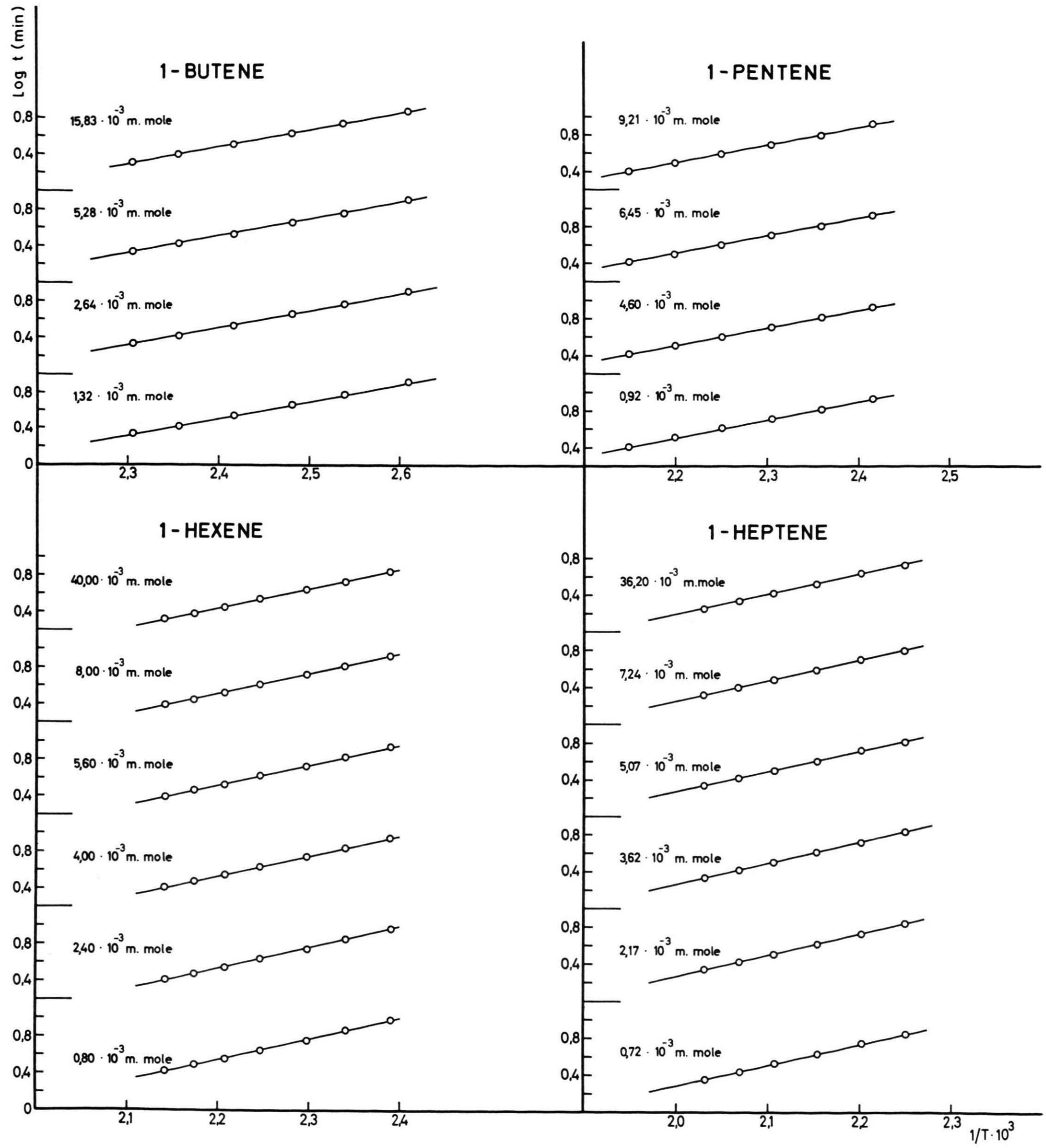

Fig. 1. Plots of decimal logarithms of retention times t (min) vs. reciprocal absolute temperature T for 1-butene, 1-pentene, 1-hexene and 1-heptene. Strictly linear plots of a similar kind were obtained with all other adsorbates.

units are the O^{2-} and Al^{3+} ions. The cation layer is generally screened by the larger anions, according to the Verwey model [12–15]. By strong activation of the surface, clusters of oxygen vacancies can be formed and some of the Al^{3+} cations are deprived of the anionic screen, thus constituting defect structures which might accommodate lone electron pairs as well as π-electron systems. This accounts for the very high heat of hydration of ceramic oxides (Al_2O_3, MgO, TiO_2, ThO_2 [16, 17]), and for the high

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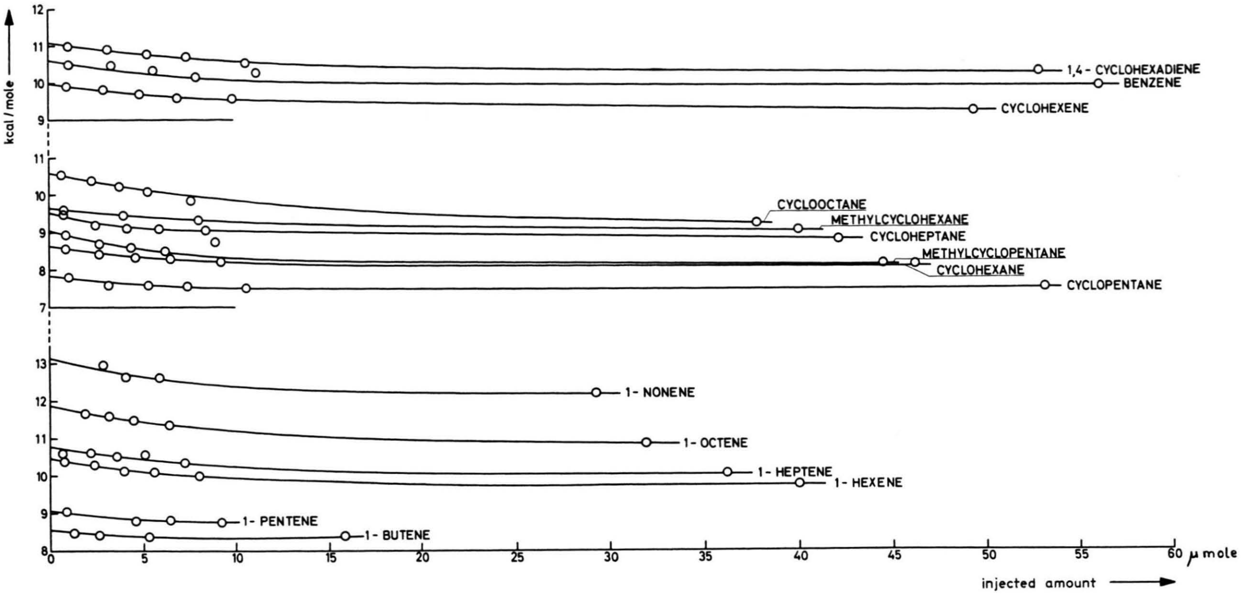

Fig. 2. Change of the chromatographic heat of adsorption with injected sample size.

interaction energy of the Lewis bases on strongly activated γ-Al_2O_3 [18, 19]. By weak activation, such that only a part of the chemisorbed water is removed [20], Lewis acid centers are lacking, and specific interactions are limited to Brønsted acid centers, e. g., the partly protonized surface hydroxyls enable to form weakly hydrogen-bonded π-complexes with non polar electron donor molecules (olefins, cyclo-olefins, aromatic hydrocarbons, etc. [21]).

These arguments seem to be supported by the present experimental results. From the plots of Q_a as a function of the number of carbon atoms, n_C, (Fig. 3) a significant increase in the heats of adsorption for 1-mono-olefins, as compared with the corresponding n-alkanes, is apparent especially with the lower terms. The effect, however, is always less remarkable than that observed by Spannheimer and Knötzinger for the pair cyclo-hexene/cyclo-hexane (difference ranging from 4.0 to 5.3 kcal/mole). This is a consequence of the much milder activation conditions employed in this work and confirms that in our case BAC are mainly responsible for interaction with the ethylenic π-electron system. The corresponding contribution seems to lower down with increasing chain length (Fig. 3). With the longest chains, the adsorption position might be less favourable for specific interactions, either as a consequence of a larger separation distance between the involved groups (due to remote location of some hydroxyls, e. g. those in pores [22]) or caused by interposition of the longer non reactive paraffinic section.

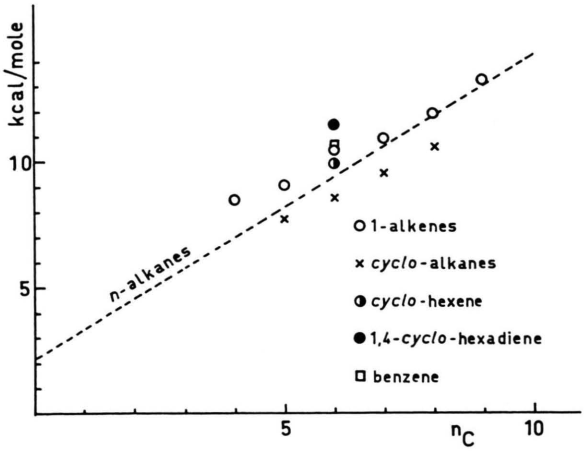

Fig. 3. Heat of adsorption (at zero coverage) as a function of the carbon atoms number, n_C, for different hydrocarbon series.

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From the sequence cyclo-hexane, cyclo-hexene, 1.4-cyclo-hexadiene (Table 3) the very remarkable constancy of the double bond contribution (1.40 to 1.50 kcal/mole) can be observed; this value agrees well with that shown by a linear alkene of chain length approaching the principal dimension of the above cyclic molecules. This is the case of 1-butene (ΔQ_a: 1-butene − n-butane = 1.48 kcal/mole). The weaker interaction in the benzene case ($Q_a = 10.60$ kcal/mole, only slightly higher than the Q_a for cyclo-hexene) can be accounted for by the resonance stabilization of the aromatic ring.

Adsorbate	Q_a	Adsorbate	Q_a
1-butene	8.56	1.4-cyclohexadiene	11.50
1-pentene	9.10	benzene	10.60
1-hexene	10.50	cyclopentane	7.85
1-heptene	10.80	methyl-cyclopentane	9.05
1-octene	11.90	methyl-cyclohexane	9.65
1-nonene	13.15	cycloheptane	9.55
cyclohexane	8.60	cyclooctane	10.60
cyclohexene	10.00		

ΔQ_a (cyclohexene − cyclohexane) = 1.40; ΔQ_a (cyclohexadiene − cyclohexene) = 1.50; ΔQ_a (1-butene − n-butane[1]) = 1.48.
ΔQ_a (methylcyclopentane − cyclopentane) = 1.20;
ΔQ_a (methylcyclohexane − cyclohexane) = 1.05.

Table 3. Heats of adsorption (kcal/mole) at zero coverage for some unsaturated and cyclic hydrocarbons on γ-Al_2O_3.

The cyclo-alkanes

The heats of adsorption of the cyclic paraffins are always lower than those of the n-alkanes with the same n_C (Fig. 3); this could be generally accounted for by the following reasoning. If a cyclo-alkane molecule is large enough to allow a quasi-planar arrangement of the carbon ring (with a minimum strain), the adsorption positions of its CH_2 groups are approximately equivalent to that of CH_2 in an open paraffinic chain. Then, the difference in the adsorption energy of such a molecule and of the corresponding n-alkane should be only due to the substitution of two CH_3 groups with two CH_2 groups. As a rough approximation this might be the case for cyclo-octane. In the previous paper[1] it was found that the adsorption potential (due to dispersion forces only) of a group i (CH_3 or CH_2) can be given by

$$P_{\text{ads, i}} = D\,\alpha_i \tag{1}$$

where D is a constant for the adsorbent and for the considered adsorbate family, and α_i is the electronic polarizability of the group. Then the total adsorption potential for the hydrocarbon can be expressed as

$$P_{\text{ads}} = 2\,D(\alpha_{CH_3} - \alpha_{CH_2}) + n_C\,D\,\alpha_{CH_2} \tag{2}$$

and the heat of adsorption (employing the suggested approximation[23] $Q_a = P_{\text{ads}} + R\,T$):

$$Q_a = 2\,D(\alpha_{CH_3} - \alpha_{CH_2}) + R\,T + n_C\,D\,\alpha_{CH_2} \tag{3}$$

where the sum of the first and second term of the right member stands for the intercept of the straight-line Q_a vs. n_C (dotted line in Fig. 3), and the first term alone is twice the difference in adsorption energy between one CH_3 and one CH_2 group. Employing the value of the above intercept found for n-alkanes (2.12 kcal/mole[1]) and considering an average temperature of 450 °K, we obtain for $2\,D\,(\alpha_{CH_3} - \alpha_{CH_2})$ the value of 1.22 kcal/mole which is in fairly good agreement with the difference now observed between the heats of adsorption of n-octane and cyclo-octane (1.15 kcal/mole).

With cyclo-alkanes having a lower n_C, greater complications are involved, mainly due to the non-planarity of the C skeleton. Some CH_2 groups will be at a larger distance from the surface as compared to aliphatic CH_2, and others at a smaller one, thus exerting opposite effects on the adsorption potentials. These effects, superimposed to that resulting from the substitution $2\,CH_3 \rightarrow 2\,CH_2$, actually make of little significance a direct comparison of the adsorption energies for cyclo-alkanes and n-alkanes with a smaller n_C value.

Finally, it can be observed that the differences between the Q_a's of methyl-cyclopentane and cyclo-pentane (1.20 kcal/mole) and of methyl-cyclohexane and cyclohexane (1.05 kcal/mole) are comparable with the average increment of the adsorption potential for each CH_2 group in n-alkanes (1.21 kcal/mole[1]).

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