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Abstract

Full Text

PHYSICAL CHEMISTRY

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ADSORPTION CAPACITY AND CATALYTIC ACTIVITY OF PLATINIZED CARBON IN THE ADDITION OF CERTAIN SILICON HYDRIDES TO UNSATURATED COMPOUNDS

(Presented by Academician A. A. Balandin on September 17, 1960)

As was noted in works (1-3), in the reactions of addition of alkyl- and chloroalkylsilanes to 1,1,2-trifluoro-2-chloroethyl allyl ether ($CH_2{=}CHCH_2OCF_2CHFCl$) and 1,1,2,2-tetrafluoroallyl ether ($CH_2{=}CHCH_2OCF_2CHF_2$), the forces of adsorption interaction of the reacting molecules with the catalyst surface may play an important role. In order to verify this, we studied the adsorption capacity of a Pt/C catalyst (1% Pt) with respect to the following alkyl- and chloroalkylsilanes: $(C_2H_5)_3SiH$ (I), $CH_3(C_2H_5)_2SiH$ (II), $C_2H_5(C_3H_7)_2SiH$ (III), Cl_3SiH (IV), $C_2H_5SiHCl_2$ (V), and $CH_3(C_2H_5)SiHCl$ (VI).

Fig. 1. Kinetic curves of adsorption of silicon hydride vapors on 1% Pt/C at 20°. The numbers on the curves here and in Fig. 2 correspond to the numbers of the compounds in Table 1.

The adsorption of these substances was studied in a flow apparatus (4) at atmospheric pressure and 20° over the range of relative vapor pressures from 0 to 0.5. Nitrogen from a cylinder, dried and purified of impurities with silica gel and activated carbon, was used as the carrier gas. Before the adsorption measurements, the catalyst was heated at 300° in vacuum ($\sim 10^{-4}$ mm) to remove adsorbed moisture and vapors of organic compounds. The saturated vapor pressures (P_s) of the adsorbates (I)–(VI), necessary–

Fig. 2. Adsorption isotherms of silicon hydride vapors on 1% Pt/C at 20°

Figure 2: Fig. 2. Adsorption isotherms of silicon hydride vapors on 1% Pt/C at 20°

required for constructing the adsorption isotherms were determined on the same apparatus by the gas-saturation method (^{5}).

At a sufficiently low flow rate of the carrier gas passing through the adsorbent, the rate of adsorption is limited by the supply of vapors of the adsorbed substance to the catalyst charge. The amount of adsorbed vapor will be proportional to the time during which the vapor-gas mixture is passed through the catalyst layer. Thus it is possible to determine P_s from the amount of adsorbed vapor and the volume of carrier gas that has passed through the system. The vapor pressure (P_s) is found from the relation: $P_s/P = v/V$, where P is the total (atmospheric) pressure in the system, v is the volume, per unit time, of substance evaporated, calculated according to the gas laws from the weight of the adsorbed substance, and V is the total volume of the mixture, calculated by measuring the flow rate with rheometers.

Fig. 2. Adsorption isotherms of silicon hydride vapors on 1% Pt/C at 20°

As can be seen from Fig. 1, the adsorption magnitude of all alkylsilanes depends linearly on the time during which the flow is passed. The kinetic curves were measured at a flow rate passing through the adsorbent of $v_1 = 1$ ml/min and a diluting-flow rate of $v_2 = 20$ ml/min. The values of P_s calculated from these data are presented in Table 1. For comparison, the values of P_s calculated by the Hass and Newton method and by the Antoine equation (^{5}) are also given there. Agreement of all values is quite satisfactory, taking into account the relatively low accuracy of determining P_s by calculation methods from the boiling point and by the experimental method, in which the accuracy of determining v_1 and v_2 with rheometers was ~ 0.1 ml/min.

Table 1

Nos. of compounds	Silicon hydride	Mol. weight	b.p., °C	P, mm	P_s (at 20°), exper.	P_s (at 20°), calc. by Hass and Newton method	P_s (at 20°), calc. by Antoine equation
I	$(C_2H_5)_3SiH$	116.28	107.0	745	27.0	28.1	29.1
II	$CH_3(C_2H_5)_2SiH$	102.25	78.0	748.5	83.4	80.3	84.0
III	$C_2H_5(C_3H_7)_2SiH$	126.19	152.5	754	33.0	33.4	36.4

Nos. of compounds	Silicon hydride	Mol. weight	b.p., °C	P, mm	P_s (at 20°), exper.	P_s (at 20°), calc. by Hass and Newton method	P_s (at 20°), calc. by Antoine equation
IV	Cl_3SiH	135.47	31.8	766	467.8	498.5	495.0
V	$C_2H_5SiHCl_2$	129.07	76.0	770	86.9	91.8	91.1
VI	$CH_3(C_2H_5)SiHCl$	108.65	69.0	769	114.0	121.2	120

In Fig. 2 the adsorption isotherms of the studied substances in in—

interval P/P_s from 0 to 0.5. The values of P/P_s were calculated by formula (4):

$P/P_s = v_1/(v_1 + v_2 - v_2 \cdot P_s/P_a)$, where P_a is atmospheric pressure. The adsorption capacity (a.c.) of the substances is not the same. Chloroalkylsilanes are adsorbed on the catalyst noticeably more strongly than alkylsilanes. In order of increasing a.c., the substances are arranged in the following sequence:

$$\mathrm{VI} > \mathrm{IV} > (\mathrm{V}) > \mathrm{II} > \mathrm{I} > \mathrm{III}.$$

A quantitative estimate of the a.c. of the indicated compounds is conveniently made by comparing the effective areas ω_0 occupied by the molecules in a densely packed adsorbed layer. The calculation of ω_0 was carried out according to the BET equation and on the basis of the known ω_0 for the benzene molecule (40 Å).

The data on the a.c. of the compounds may be compared with their reactivity in competing addition reactions to 1,1,2-trifluoro-2-chloroethyl allyl ether (see Table 2). Comparison of these data shows that,

Table 2

Nos.	Components	Nos. of compounds according to Table 1	Yield, %	Relative activity	ω_0 (Å^2)
1	Cl_3SiH	IV	42		50
1	$C_2H_5SiHCl_2$	V	42	1	50
2	Cl_3SiH	IV	20		50
2	$(CH_3)(C_2H_5)_2SiH$	II	33	1.7	58
3	Cl_3SiH	IV	31		50
3	$(C_2H_5)_3SiH$	I	51	1.7	64

Nos.	Components	Nos. of compounds according to Table 1	Yield, %	Relative activity	ω_0 (Å^2)
4	Cl_3SiH	IV	29		50
4	$(C_2H_5)(C_3H_7)_2SiH$ *	III	63	2.2	70
5	Cl_3SiH	IV	32		50
5	$(CH_3)(C_2H_5)SiHCl$	VI	35	1.1	40
6	$C_2H_5SiHCl_2$	V	27		50
6	$(CH_3)(C_2H_5)SiHCl$	VI	33	1.2	40
7	$C_2H_5SiHCl_2$	V	25		50
7	$(CH_3)(C_2H_5)_2SiH$	II	47	1.9	58

* Analysis of the gas phase ($\sim$ 200 cm^3) of the products of this experiment showed that it consists of 96% hydrogen. The formation of hydrogen is evidently associated with recombination of H atoms formed upon homolytic cleavage of the Si—H bond:

$$\equiv \text{Si—H} \rightarrow \equiv \text{Si} + \text{H}.$$

when one and the same compound (IV or V) is used in a mixture, the yield of the addition product of the second component increases with increasing ω_0 (i.e., with decreasing a.c.). This is observed for the mixtures IV + II, IV + I, IV + III and V + VI, V + III. In addition, for substances with practically identical a.c. (IV + V), the yield of addition products is also the same.

The influence of adsorption-interaction forces in competing addition reactions, taking into account the conclusions drawn in work (3), may be interpreted as follows. The increased a.c. of chlorine-containing silicon hydrides leads to the formation on the surface of very active chlorosilyl radicals (Cl_3Si and $Cl_2SiC_2H_5$), which, by abstracting hydrogen from a trialkylsilane, lead to the formation of a less active trialkylsilyl radical. The latter then add to the multiple bond of the unsaturated compound. At the same time, evidently, direct addition of chlorosilyl radicals to the unsaturated compound also takes place. In the competing additions of $(CH_3)(C_2H_5)(Cl)SiH$ with Cl_3SiH and $C_2H_5SiHCl_2$, the picture changes somewhat. The increased a.c. and the lower (than in Cl_3SiH and $C_2H_5SiHCl_2$) energy of the Si—H bond in $(CH_3)(C_2H_5)(Cl)SiH$ account for the preferential formation on the surface of the radical $(CH_3)(C_2H_5)(Cl)Si$. However, this radical cannot so readily abstract hydrogen atoms from Cl_3SiH and $C_2H_5SiHCl_2$, where the hydrogen is more strongly bound to silicon. Therefore, the predominant direction of reaction of the radical $(CH_3)(C_2H_5)(Cl)Si$ is addition to the multiple bond of the unsaturated compound. Thus, despite the increased a.c., $(CH_3)(C_2H_5)(Cl)SiH$ will in this case nevertheless add more preferentially than Cl_3SiH or $C_2H_5SiHCl_2$.

The considerations set forth above concerning the ease with which chlorosilyl radicals capture hydrogen atoms of Si—H bonds and the distinctive chain transfer are evidently also applicable to the intermediate radicals that are formed, $X_3Si\dot{C}H_2\dot{C}H—R$ ($X = Cl$, alkyl group, $R = CH_2OCF_2CFClH$).

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