REACTIONS ON A SURFACE.

2.* ROLE OF OXIDES IN CONDENSATION OF 3-METHYL-3-BUTEN-1-OL WITH ALDEHYDES AND KETONES*

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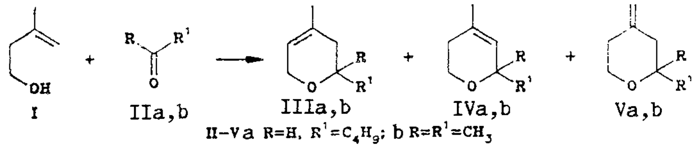
The formation of di- and tetrahydropyrans on an oxide surface in the reaction of 3-methyl-3-buten-1-ol with carbonyl compounds is due primarily to the adsorptive properties of the surface itself, Lewis acid centers hardly catalyzing this reaction at all under the conditions being considered.

We have shown previously [1] that the reaction of 3-methyl-3-buten-1-ol (I) with carbonyl compounds on an SiO_2 or Al_2O_3 surface (in the solid phase) leads to derivatives of di- and tetrahydropyrans. In the present work, experiments were undertaken to explain the role of the oxides in this reaction. To that end, we carried out the condensation of alcohol I with carbonyl compounds IIa, b on the surfaces of various oxides and carbon.†



II-Va $R=H$, $R'=C_4H_9$; b $R=R'=CH_3$

The condensation of γ-unsaturated alcohols with carbonyl compounds is catalyzed by acidic agents [2]. It may be assumed that in the absence of protons, the course of the reaction is facilitated by the presence of Lewis acid centers on the oxide surfaces. Although Al_2O_3 is more acidic in nature than SiO_2, the basic formation of substituted 4-hydroxytetrahydropyrans takes place on it with an insignificant yield [1].

The acidic properties of Fe_2O_3 and NiO are quite marked. Moreover, unlike Al_2O_3, they can be completely dehydrated at 400°C without a structural change. However, reactions on their surfaces proceed sluggishly (Table 1, runs 5-8). It is possible to preclude completely the influence of acid centers by, for example, using alkaline earth metal oxides. It turns out, however, that the yield of reaction products on CaO is rather high (runs 9 and 10). In addition, compounds III-Va are formed on this oxide with a yield of 22% of the corresponding 4-hydroxytetrapyrans.

On an SiO_2 surface, there are silanol groups that selectively adsorb polar molecules through the formation of hydrogen bonds. Dehydration, with the formation of Si—O—Si bonds, starts at temperatures above 200°C and is completed at 600°C [3]. Therefore, we used SiO_2 calcined at 400°C so that some of the silanol groups on its surface were preserved. The results of runs made on different SiO_2 samples dried to constant weight at 200, 400, and 600°C (runs 1-3) show that in the presence of silanol groups, both the conversion of alcohol I and the yield of reaction products is low.

Thus, neither acidic properties of the oxides nor special structural features of the SiO_2 are the driving force of the reaction carried out under our conditions. Apparently, when polar compounds are adsorbed on the active centers discussed, quite stable products are formed which do not take part in further conversions. Consequently, in those cases when a reaction does go, weaker, physical adsorption is dominant. This is confirmed by the fact

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*See [1] for Communication 1 of the series.

†It was possible to improve the procedure for treating the reaction mass and the analysis compared to the work in [1].

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TABLE 1. Condensation of Alcohol I with Compounds IIa, b on Oxide Surface (20 h, 20°C, oxide:reagent = 10:1 by weight)

Run No.	Solid phase	Compound II	Conversion of alcohol I, %	Isomer ratio, III:IV:V	Yield of products III-V, based on the alcohol I converted %
1[*1]	SiO_2	a	64	34 : 23 : 43	61
2[*2]	SiO_2	a	90	34 : 20 : 46	94
3[*3]	SiO_2	a	91	32 : 29 : 39	94
4[*4]	SiO_2	a	91	33 : 21 : 46	94
5	Fe_2O_3	a	20	—	5
6	Fe_2O_3	b	20	—	5
7	NiO	a	19	—	10
8	NiO	b	18	—	17
9	CaO	a	23	—	9
10	CaO	b	32	—	43
11		a	82	41 : 22 : 37	94
12	NaA (4 Å)	a	77	38 : 25 : 37	82
13		b	41	1 : 43 : 56	83
14[*5]	" "	a	76	36 : 26 : 38	84
15	Al_2O_3/SiO_2	a	94	45 : 24 : 31	75
16	Al_2O_3/SiO_2	b	84	1 : 54 : 45	60

[*1] Oxide calcined at 200°C.
[*2] Oxide calcined at 400°C.
[*3] Oxide calcined at 600°C.
[*4] Oxide calcined again after run 2.
[*5] Zeolite calcined again after run 12.

that both the starting compounds and reaction products are easily extracted by ordinary treatment with acetone, and the water evolved during the reaction has to be removed by calcination again at 400°C. The yield of pyran derivatives and the conversion of the alcohol on recalcined oxides is practically unchanged (runs 2 and 4, 12 and 14), while the reaction does not go without thermal treatment because the chemisorbed water substantially blocks adsorption of the starting compounds.

The reagents can be activated through adsorption either in pores or in the cells of the oxide crystal lattice. Activated carbon is an amorphous, inert carrier with a developed surface on which there are virtually no active centers. In this case, adsorption takes place in pores. Consequently, carbon is a good model for the estimation of the role of physical adosrption in this reaction. It turned out that the yield of products on activated carbon (run 11) was markedly greater than when oxides (other than SiO_2) were used, reaching 94%. Thus, the presence of a developed surface is a sufficient condition for the reaction under consideration to occur. This agrees well with results obtained on SiO_2, which has the largest specific surface [4] of all the oxides used.

Zeolites, having a strictly defined pore size, can adsorb only those molecules that can pass through their crystal lattice [4]. In order to avoid the effect of acid centers, we used zeolites in the salt form. It turns out that on type NaA zeolite, with a 3 Å pore size, the condensation of alcohol I with aldehydes or ketones scarcely takes place at all. Then, when the pore size is increased to 4 Å, one obtains the reaction products of alcohol I with either pentanal or acetone in high yield (82% and 83%, respectively) (runs 12 and 13). Cyclohexane also condenses with alcohol I under analogous conditions, albeit less easily (a 45% yield per converted cyclohexane), even though according to its size it cannot be adsorbed by this type of zeolite. Apparently, the reaction occurs on the surface of the zeolite, but the zeolite pore size cannot be less than 4 Å in order that the molecules of the starting compounds be oriented in the necessary way, even though not adsorbed.

The size of the unit cells in the crystal lattices of Fe_2O_3 and NiO is less than 4 Å [5], consequently adsorption or orientation as on zeolite NaA (4 Å) is precluded here. In view of the fact that their specific surfaces are also small, the low yield of reaction products is fully understandable.

Aluminosilicates are similar to zeolites in composition, but unlike them do not have a strictly defined pore size. They have a rather well-developed surface, although it is less than that of activated carbon and silica gel. One would expect the yield of reaction products when aluminosilicate is used to be greater than on Fe_2O_3 and NiO, but less than on SiO_2 and activated carbon. The results of runs 15 and 16 confirm this assumption.

From the accumulation of data discussed, it follows that the condensation of alcohol I with carbonyl compounds IIa, b actually becomes possible under our conditions thanks to the physical adsorption of the compounds on the oxide surfaces.

EXPERIMENTAL

The reaction products were identified by comparing retention times with those of samples obtained by known procedures [2, 6-8]. GLC analyses were carried out on an LKhM-8MD instrument (FID, 2000 × 3 mm column, 15% PEGA on Chromosorb P, nitrogen carrier gas, 40 ml/min flow rate).

All oxides and carbon were slowly heated in a muffle furnace to 400°C and held at this temperature for 3 h. After being cooled in a desiccator over $CaCl_2$, the samples were ground and the 0.05-0.12 mm fraction selected.

The starting reagents were dried over NaA molecular sieves (3 Å).

2-Butyl-4-methyl-3,6-dihydro-2H-pyran (IIIa), 2-Butyl-4-methyl-5,6-dihydro-2H-pyran (IVa), and 2-Butyl-4-methylenetetrahydropyran (Va). Into a 50 ml flask with a ground glass stopper are placed, in order, 17.2 g SiO_2, 0.86 g (10 mmole) alcohol I, and 0.86 g (10 mmole) aldehyde IIa. The flask is shaken and allowed to stand for 20 h at 20°C. The reaction mass is then washed with acetone (3 × 25 ml), filtered, a standard (in the case of compound IIa, undecane, and of IIb, decane) added, and analyzed by GLC. Yield (calculated for the converted alcohol I) 94% (run 2). The remaining runs were carried out in an analogous way.

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