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Organic Polymers: Correlation between Their Structure and Catalytic Activity in Heterogeneous Systems

III. Acid-type Catalysis, Sulfonated and Phosphonated Polyphenyl*

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Sulfonated and phosphonated polyphenyl are ion exchangers of high thermal stability and can be used as heterogeneous catalysts for reactions in the vapor phase at elevated temperature. If they are impregnated with NaOH solution, catalytic activity is seen to decrease gradually, and if a quantity of NaOH is used equivalent to the amount of SO_3H groups as calculated from the microanalytical data, no catalytic activity is found for any of the reactions studied. Unlike neomenthol which gives almost exclusively *p*-menth-3-ene on dehydration, menthol gives some *p*-menth-2-ene as well. Product distribution in the vapor-phase reaction is almost identical with that observed in the liquid-phase dehydration catalysed by *p*-toluenesulfonic acid and phosphoric acid. Isomerization of butene-1 into butene-2 shows a slight preference for the formation of *cis*-butene-2. On the whole the behavior of the substrates in the vapor phase is not much different from that in the liquid phase under conditions of acid catalysis, and no special surface effects need to be assumed.

INTRODUCTION

The fact that the acidity of a surface can be an important factor in some types of heterogeneous catalytic reactions has been known for some time. Carbonium ions were shown to be intermediates in the cracking of hydrocarbons over silica-alumina catalysts (*1*), and the cause of the surface acidity has been adequately explained (*2*). It has also been extensively shown that the dehydration of alcohols and isomerization of olefins over pure alumina can be accounted for by the acidity of the surface (*3*). Moreover, many reactions which can be promoted by acids in solutions, can be catalyzed heterogeneously by acid-type ion exchangers (*4*). The acidity of conventional ion exchangers can be interpreted quite well, the behavior of the sulfonyl and carboxyl groups in solution is well known, and parallels between surface and solution catalysis can easily be drawn. Unfortunately, the known commercial ion exchangers are unstable above 150°, which precludes their use as catalysts in most vapor-phase reactions.

The interpretation of the acidity of conventional catalysts has met with some trouble however. Some workers have tried to interpret the acid strength of a surface by its ability to donate protons to different bases (*5*). The main disadvantage of this method in catalytic research is the fact that the measurement cannot be performed at the temperature of the catalytic reaction itself. To overcome this difficulty, attempts have been made to measure the adsorption of amines at elevated temperatures. However, no satisfactory agreement could be

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* Part II in the series: J. Manassen and Sh. Khalif, *J. Am. Chem. Soc.* 88, 1943 (1966).

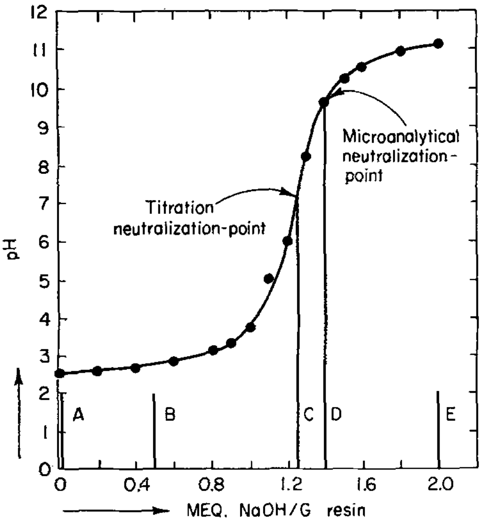


FIG. 1. Titration curve of 0.1-g portions of sulfonated polyphenyl with 0.1 *N* NaOH. The letters A to E indicate the degree of neutralization of the different catalysts used.

obtained with catalytic activity by this method, and this was explained by the heterogeneity of the surfaces in question, containing centers of different acid strengths (*6*).

In the present paper we present results of catalytic vapor-phase reactions obtained with specially synthesized organic ion exchangers, which combine the advantages of thermal stability with an easy interpretation of the acidic centers.

CATALYSTS

It has been shown recently how benzene may be polymerized into a perfectly stable insoluble polyphenyl with the help of a Lewis acid-oxidant system (*7*). In the experimental section we describe how this polymer can be either sulfonated or phosphonated heterogeneously with the formation of ion exchangers, which do not show any change on heating to temperatures as high as 350°C. They can be titrated by the conventional method of shaking aliquots in dilute salt solution with different quantities of sodium hydroxide solution (*8*). Figures 1 and 2 show the curves obtained with sulfonated and phosphonated resins, respectively. They are quite similar to those published in the literature for conventional sulfonic and phosphonic exchangers (*9*).

From the microanalytical data the percentage of sulfonyl and phosphonyl groups can be calculated, and they are indicated in the figures as microanalytical neutralization points. In the case of the sulfonic acid this can be seen not to coincide with the titration neutralization point. In the case of the phosphonic acid it is impossible to define the titration neutralization point with sufficient accuracy. (Untreated polyphenyl gives a pH of 11 after the first drop of 0.1 *N* NaOH is added.) The following

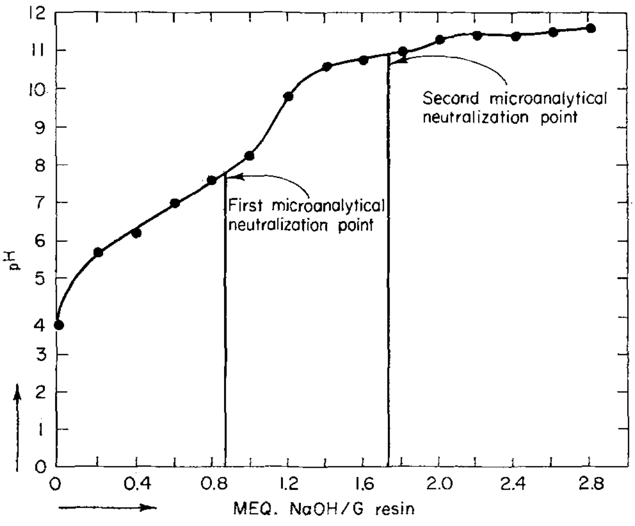


FIG. 2. Titration curve of 0.1-g portions of phosphonated polyphenyl with 0.1 *N* NaOH.

catalysts were prepared by NaOH impregnation of the sulfonated polyphenyl (SPB):

SPB A: Nonimpregnated
SPB B: Impregnated with NaOH sufficient to neutralize about one-third of sulfonyl groups
SPB C: Impregnated with a quantity of NaOH conforming to the titration neutralization point
SPB D: Impregnated with a quantity of NaOH conforming to the microanalytical neutralization point
SPB E: About one-third excess NaOH used

Other catalysts

PPB: Nonimpregnated phosphonated polyphenyl
PB: Untreated polyphenyl

Results

Because the catalysts were seen to be deactivated rapidly, especially with the olefinic reagents, presumably by polymeric products, a rigid schedule had to be followed for comparing the respective activities. The materials were pressed in 1-g quantities as pellets of 1-inch diameter at a pressure of 4000 psi. The pellets were crushed and sieved between 12/25 mesh sieves and heated at 350° for 1-hr in a nitrogen stream of 20 ml/hr. After cooling, 1-g quantities were taken for the reactions. A 1:1 menthol/cyclohexane mixture was passed first at three different temperatures, 1 ml at each temperature. After that 1 ml of a 1:1 neomenthol/cyclohexane mixture was passed at one temperature only, followed by undiluted menthene-1 at three different temperatures, 1 ml each. The lower limit of the temperature used was determined by the boiling point of the materials in question, as we wanted to study the heterogeneous *vapor*-phase reaction. Reactions were always started at the lowest temperature. The butene isomerization was studied on a fresh catalyst sample at a rate of 10 ml/min, half an hour for each temperature.

Table 1 gives the dehydration results; a consistent feature is the fact that under all conditions the menthene-2/menthene-3 ratio is much higher in the case of the menthol than in that of neomenthol. The latter is seen to react about four times as rapidly as menthol. Catalyst C, which conforms to the titration neutralization point, shows an appreciable activity, contrary to catalyst D, which conforms to the microanalytical neutralization point and which is totally inactive. That the sulfonyl and the phosphonyl groups are responsible for the reaction in question can be seen

TABLE 1
THE DEHYDRATION OF MENTHOL AND NEOMENTHOL OVER DIFFERENT CATALYSTS[a,b]

		% Reaction[d]				Ratio menthene-2/menthene-3			
Catalyst[c]	Alcohol	230°	250°	300°	350°	230°	250°	300°	350°
SPB A	M	84	—	—	—	11:89	—	—	—
	N	89[e]	—	—	—	3:97	—	—	—
SPB B	M	15	28	68	—	18:82	18:82	19:81	—
	N	25[e]	—	—	—	3:97	—	—	—
SPB C	M	—	16	57	65	—	18:82	20:80	21:79
	N	—	—	25[f]	—	—	—	5:95	—
PPB	M	32	42	62	—	25:75	25:75	22:78	—
	N	20[e]	—	—	—	2:98	—	—	—

[a] A 1:1 mixture of menthol and cyclohexane was passed at a liquid rate of 4.5 ml/hr.

[b] Weight of catalyst: 1 g.

[c] Catalysts SPB D, SPB E, and PB are inactive towards menthol as well as neomenthol under all conditions studied.

[d] The percentage of the alcohol that has reacted. At higher conversion olefins other than menthene-2 and menthene-3 are also found.

[e] A 1:1 mixture with cyclohexane at 18 ml/hr.

[f] A 1:1 mixture with cyclohexane at 9 ml/hr.

TABLE 2
PRODUCT RATIO IN THE DEHYDRATION OF MENTHOL AND NEOMENTHOL UNDER DIFFERENT CONDITIONS

	SPB-B[a] $T = 230°$		PPB[a] $T = 230°$		2 N p-toluene sulfonic acid solution[b] $T = 140°$		2 N phosphoric acid solution[b] $T = 194°$	
	Conversion (%)	Ratio menthene-2/-3	Conversion (%)	Ratio menthene-2/-3	Conversion (%)	Ratio menthene-2/-3	Conversion (%)	Ratio menthene-2/-3
Menthol	10	18:82	4	24:76	8	29:71	4	32:68
	14	18:82	10	24:76	26	32:68	25	31:69
	40	17:83	45	25:75	85	33:67	76	32:68
	78	17:83	90	23:77				
Neomenthol	25	3:97	20	2:98	8.5	0:100	7.5	0:100

[a] A 1:1 mixture of alcohol and cyclohexane was passed at liquid rates ranging from 0.8–18 ml/hr over 1 g of catalyst.

[b] A 1:1 mixture of alcohol and cyclohexane (0.5 ml) was shaken in a closed ampoule together with 5 ml of 2 N acid solution. Reaction times from 0.25–15.5 hr.

from the inactivity of the untreated polybenzene.

Table 2 shows that the higher percentage of menthene-2 found in the case of menthol is not caused by a subsequent isomerization of menthene-3 initially formed, and compares the ratios found over SPB and PPB with those from dehydrations in p-toluenesulfonic acid and phosphoric acid solutions, respectively. From Table 3 it can be seen that racemization is the most rapid reaction of menthene-1 and that, contrary to catalyst C, catalyst D is entirely inactive. Table 4 gives the results of the butene isomerizations, which could be studied at lower temperatures because of its low boiling point. The main feature is a slight preference for *cis*-butene-

TABLE 3
ISOMERIZATION AND RACEMIZATION OF + 1-p-MENTHENE OVER DIFFERENT CATALYSTS[a,b]

	% Conversion into different products				% Racemization			
Catalyst	200°	250°	300°	350°	200°	250°	300°	350°
SPB A	28	50	62	—	100	100	100	—
SPB B	—	26	43	50	—	100	100	100
SPB C	—	10	15	17	—	58	87	84
P.P.B.	—	19	53	61	—	59	83	100

[a] Liquid rate: 4.5 ml/hr, 1 g of catalyst.

[b] Catalysts SPB D, SPB E, and PB were inactive under all conditions studied.

TABLE 5
RATIO OF *cis* TO *trans*-BUTENE-2 ON REACTION OF BUTENE-1 OVER PHOSPHONATED POLYPHENYL[a]

% Butene-1 reacted	Ratio *cis/trans*
Less than one	1.65
4	1.49
9	1.49

[a] $T = 200°$; 1 g of catalyst. Gas velocities ranging from 5–20 ml/min.

TABLE 4
ISOMERIZATION OF BUTENE-1 OVER DIFFERENT CATALYSTS[a,b]

	% Conversion into butene-2									
	$T = 100°$		$T = 150°$		$T = 200°$		$T = 250°$		$T = 300°$	
Catalyst	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
SPB A	4.8	4.8	15.3	14.9	35.6	26.2	—	—	—	—
SPB B	—	—	—	—	3.5	4.0	9.9	11.0	18.5	18.8
PPB	—	—	—	—	4.1	5.7	19.5	19.5	38.0	29.0

[a] 1g of catalyst. Gas velocity, 10 ml/min.

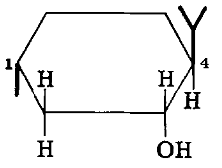
[b] Catalysts SPB C is slightly active at 350°; SPB D, SPB E, and PB are inactive under all conditions studied.

2 at low conversion of the butene-1, which is more outspoken in the case of the phosphonated resin. Table 5 gives the *cis/trans* ratio of the butene-2 formed for different conversions at one temperature.

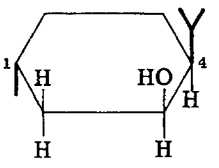
DISCUSSION

Menthol–Neomenthol

Use of the two stereoisomeric alcohols menthol and neomenthol may indicate whether the elimination occurs from H and OH groups situated *cis* or *trans* relative to one another.



Menthol



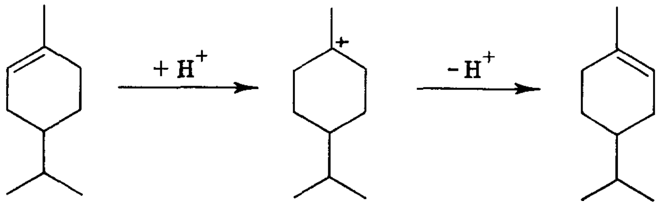
Neomenthol

In this kind of acid-catalyzed elimination with hydroxyl as the leaving group, double-bond formation may be expected on the side of the most substituted carbon atom, which would give menthene-3. A preference for *trans* elimination on the other hand would give menthene-2 in the case of menthol and menthene-3 in the case of neomenthol. These two substrates have been used to study the direction of elimination over alumina where preference for *trans* elimination was found (*10*). The fact that in the present work different product ratios are found for the two alcohols, excludes a classical carbonium ion as the intermediate in at least one of the two reactions, as both would give the same ion. The formation of menthene-3 for neomenthol, which is found almost exclusively under all conditions, can best be accounted for by participation of the neighboring *trans* hydrogen at C_4, as could be proven in formolysis of neomenthyl tosylate (*11*). The same mechanism could account for the formation of menthene-2 from menthol. The formation of menthene-3 from menthol is more difficult to explain. In analogy with the hydrogen participation one could propose participation by the isopropyl at C_4. On dehydration of menthol under all conditions a third product was always found, which we could prove not to be a *p*-menthene. It could be 1-methyl-3-isopropylcyclohexene. We hope to elucidate this point in future work. The main conclusion to be drawn from the present results is the great similarity in product distribution between the heterogeneous vapor-phase reaction and the reaction in solution. The product distribution on dehydration of menthol is also very similar to that found from elimination reactions of its aryl sulfonate esters in aprotic solvents (*12*). Consequently one might propose an ester intermediate, which decomposes thermally. To check this point we prepared the menthol ester of benzenesulfonic acid. It can be heated in bulk up to 140°, after which it decomposes vigorously in what seems to be an autocatalytic reaction. If, however, the same treatment is given with the addition of a small quantity of *p*-toluenesulfonic acid, the ester decomposes in a much more controlled way at 100°, the menthene-2/-3 ratio in both cases being about equal to that found for dehydration of the alcohol. This means that the thermal decomposition of the ester is also acid-catalyzed, and consideration of an ester intermediate loses its meaning, as mechanistic pathways for acid-catalyzed ester and alcohol decomposition might be fairly similar.

In the vapor-phase reaction there is a noticeable difference in product distribution between the sulfonated and the phosphonated resin. The latter being less acidic, gives more *trans* elimination, as one would expect. In the solution reactions the contribution of *trans* elimination is even higher and there is no noticeable difference between the two acids. All the results show that the heterogeneous vapor-phase reaction behaves as we would expect from an ordinary acid-catalyzed reaction and no consideration of special "surface" effects is necessary whatsoever. One might even go further and state that the vapor-phase reaction shows the expected difference between two acids of different strength which somehow is blurred by the presence of the solvent in the case of the liquid-phase reaction. The fact that catalyst SPB C is active unlike SPB D seems to indicate that the neutralization point found by titration is not the real one. The materials in question are quite hydrophobic and in spite of long shaking times in a salt solution some of the hydrogen ions might not be forced into solution.

p-Menth-1-ene

The reason for studying the double-bond shifts in menthene-1 was the expected ease of racemization, which was indeed found and can be formally indicated as follows:



L-Menthene D-Menthene

The conversion of an olefin into its optical antipode by way of the tertiary carbonium ion can be considered as a reaction which will go at a high rate under acidic conditions and can be expected to be a sensitive test of catalyst activity. Table 3 shows this to be true. Moreover, according to this test catalyst SPB D is entirely inactive, which proves the sulfonyl groups to be responsible for the reactions in question.

Butene-1

The preferred formation of the *cis* olefin on double-bond shifts in olefins has been observed under different conditions. It is regularly found in reactions over alumina or silica-alumina (*13*), but also in 0.5 *N* perchloric acid solution (*14*). In concentrated sulfuric or phosphoric acid on the other hand, equal quantities of the two isomers are found, which is thought to be indicative of a carbonium ion intermediate (*15*). The phenomenon has never been satisfactorily explained. From Table 4 we see a small preference for *cis*-butene-2 over catalyst SPB B. The effect is somewhat more distinct with the phosphonated resin. Table 5 gives the results of olefin ratio, intentionally measured at low conversion with great accuracy, and the ratio *cis*-butene-2/*trans*-butene-2 is seen to be about 1.5 for catalyst PPB at 200°. It seems that lower acid strength promotes isomerization into the *cis* olefin in the vapor as well as in the liquid phase.

At 200° the activities of catalysts SPB B and PPB are about equal for butene isomerization. At 300° PPB is at least twice as active, which can best be explained by the smaller acid strength of the phosphoric acid, which causes the reaction to have a higher energy of activation.

Summarizing, it can be said that for the reactions of the substrates studied, acid catalysis in the vapor phase behaves as expected for acids of different strength and no specific differences from behavior in solutions can be found.

EXPERIMENTAL

Menthol and neomenthol. The menthol was a commercial product (H. E. Daniel Ltd., London) and the neomenthol was synthesized by the reduction of menthone (*10*). The final separation of neomenthol and menthol was done by column chromatography. If 5 g of a 3:7 menthol/neomenthol mixture is eluted over a column of 250 g of Merck acid-washed alumina with 1 liter of a 10% solution of ether in pentane, menthol stays on the column and neomenthol is recovered in an almost pure state from the effluent.

Polymerization of benzene. The method described in ref. (7b) was followed. It was found to be convenient to remove most of the metal ions by washing the precipitate of the polymerization reaction with methanol, before the treatment with HCl solution.

Analysis	C	H	Cl	rest
Found:	91,97	5.11	1.83	0.7
Calculated for:				
$(C_6H_4)_{98.1}(Cl)_{1.83}(rest)_{0.7}$	92.5	5.13	1.83	0.7

Sulfonation of polyphenyl. Concentrated H_2SO_4 (25 ml) was heated to 115° and 2.5 g of polyphenyl was added, with vigorous stirring. Stirring and heating were continued for 1 hr. After being cooled the mixture was poured onto ice, filtered, and washed with water. After being boiled with water the material was filtered again, washed with water, and dried at 120°. Yield 2.75 g.

Analysis	C	H	Cl	S
Found:	78.95	4.77	2.06	4.57
Calculated for:				
$(C_6H_4)_{86.6}(SO_3)_{11.34}$ $(Cl)_{2.06}$	81.90	4.55	2.06	4.57

We have no ready explanation for the low C values, except that there may be some phenolic groups on the polyphenyl.

Phosphonation of polyphenyl. A mixture of 225 ml of PCl_3, 65 g of freshly sublimed $AlCl_3$, and 7.5 g of polyphenyl was refluxed with vigorous stirring for 48 hr. The PCl_3 was removed by distillation *in vacuo* and 125 ml of dichloroethane added. The solution was saturated with chlorine at 0° while being stirred. Water (100 ml) was carefully added also at 0° and the mixture filtered. The filtrate was boiled with 18% HCl three times and with water once. The product was dried at 120°. Yield, 7.5 g.

Analysis	C	H	Cl	P	rest
Found:	77.3	4.37	5.81	2.76	2.74
Calculated for:					
$(C_6H_4)_{84.33}(PO_3H)_{7.12}$ $(Cl)_{5.81}(rest)_{2.74}$	80.0	4.33	5.81	2.76	2.74

Gas chromatography. Menthol, neomenthol, and menthene were separated on a 5-m Carbowax 20 M column by temperature programming from 75° to 200° at 11°/min. The composition of the menthene mixture was analyzed on a 5-m bis(ethylhexyl) tetrachlorophthalate column at 120° and the butene mixture over a 10 *m* bis(ethylhexyl) tetrachlorophthalate column at 0°.

Impregnation of catalysts. A weighed quantity of material was refluxed for 12 hr with the calculated volume of 0.1 *N* alcoholic NaOH and the solvent removed by evaporation.

Catalytic reaction. Reactants were introduced by means of a syringe pump into a vertically heated Pyrex tube, containing 1 g of catalyst.

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