$(OR')_2OR$, $HC(OR)_2OR'$ and $HC(OR')_3$. Only a small amount of the two mixed esters is obtained when propyl orthoformate and isoamyl orthoformate are mixed, as compared with a larger amount of the two mixed compounds using esters of lower molecular weights. This may be explained by assuming that reaction is preceded by decomposition into fragments, this decomposition being known to be less rapid in the case of the higher homologs. Similar reactions with alcohols and mercaptans seem to involve transfer of OR rather than R.

Summary

1. At room temperatures the mixed orthoformates thus far investigated isomerize to a mixture of all four possible esters, this reaction taking place almost instantaneously over phosphorus pentoxide.

2. At room temperatures two orthoformates react with interchange of radicals, the yield of products varying, as far as observation has gone, inversely as the radical weights involved.

3. Tripropyl orthoformate reacts with absolute ethyl alcohol, giving a mixture of the four possible orthoformates and two alcohols. Ethyl mercaptan reacts with triethyl orthoformate giving the mono thio compound.

BUFFALO, N. Y.

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[CONTRIBUTION FROM THOMAS AND HOCHWALT LABORATORIES, INC.]

Polymerization of Diolefins with Olefins. II. Function of Pentene-2 in the Polymerization of Isoprene

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In the previous paper[1] it was reported that when pure isoprene, in which there was no appreciable amount of olefin present, was placed in contact with anhydrous aluminum chloride, there was no temperature rise or any other obvious chemical reaction, even when a considerable proportion of anhydrous aluminum chloride had been added. It was shown that an olefin, such as pentene-2, added to the isoprene–aluminum chloride mix, started the reaction immediately; and that in polymerizing isoprene and pentene-2 by aluminum chloride, there were two solid polymers formed, one insoluble and the other soluble in hydrocarbon solvents. The amount of the soluble polymer formed is proportional to the pentene-2 present, while the amount of the insoluble polymer varies inversely with the amount of pentene-2 present.

The purer the isoprene, the more inert it is toward aluminum chloride. Very pure isoprene can be obtained by converting it into the tetrabromide

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[1] Thomas and Carmody, THIS JOURNAL, **54**, 2480 (1932).

and regenerating it with zinc dust according to Whitby and Crozier.[2] Several hours of contact of this pure isoprene with anhydrous aluminum chloride causes the formation of small bubbles which are immediately followed by a spongy polymeric growth. A few days later there are masses of this polymer, insoluble in the water-white isoprene. The majority of the isoprene is slowly converted into this gelatinous mass, analysis of which shows it to be $(C_5H_8)_x$, identical with the insoluble polymer previously described.

Large quantities of dry hydrogen chloride, bubbled through isoprene containing aluminum chloride, cause the reaction to become violent. Fifty cc. of isoprene in 250 cc. of naphtha was stirred rapidly in a cooled vessel while 10 g. of aluminum chloride was added in portions. A slow stream of dry hydrogen chloride gas was led below the surface of the mixture and polymerization was continued for three and one-half hours, after which the polymers were recovered in the manner previously reported. There was obtained 21 g. of soluble polymer and 12.4 g. of insoluble. Hence it can be seen that dry hydrogen chloride gas, beside initiating the polymerization of isoprene, greatly influences the yields of soluble and insoluble polymers.

Isoprene hydrochloride, formed by passing hydrogen chloride into isoprene, reacts with aluminum chloride to form a complex which is soluble in isoprene. This suggested that the soluble polymer is produced in relation to the isoprene hydrochloride present; and when enough is present to dissolve completely the aluminum chloride then only soluble polymer is produced. This point was further substantiated when it was found that only the soluble polymer was formed when isoprene hydrochloride was added to a reaction mixture of isoprene and aluminum chloride.

Other mutual solvents for isoprene and aluminum chloride increase the yield of soluble and decrease the insoluble polymers. When 5 g. of aluminum chloride is dissolved in 45 g. of nitrobenzene and this solution added to isoprene there is obtained soluble polymer only. If a diluent, such as petroleum naphtha, is used with the isoprene, the aluminum chloride is partly thrown out of solution and some insoluble polymer is obtained. Ethyl acetate forms with aluminum chloride, an isoprene soluble complex. By running a series of identical polymerizations with the exception of increasing by small amounts ethyl acetate added to the reaction mixture, it is found that there is an exact relation between yield of soluble polymer and the amount of ethyl acetate added. This relationship is much the same as when pentene-2 is added to isoprene.

It is assumed that the soluble and insoluble polymers differ in molecular weight alone, and it is evident that the more aluminum chloride put into solution, the lower the molecular weight of the polymer obtained. When

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[2] Whitby and Crozier, *Can. J. Research*, **6**, 212 (1932)

no mutual solvent for the isoprene and aluminum chloride is employed the polymerization is initiated on the surface of the catalyst. With solid aluminum chloride, the surface comparable to molecular dispersement, is small when referred to the same mass of aluminum chloride in solution as a complex. Thus, with solid aluminum chloride, not many polymer growths are started, and after prolonged contact the polymers have an opportunity to grow to large size and become insoluble. When the catalyst is in solution, giving molecular contact, many polymer growths are started and these are so numerous that with the available isoprene they do not grow to high molecular weight, thus producing the soluble polymer. This theory of short chain formation has independently been advanced by Houtz and Adkins in their work with styrene.[3]

Previous work showed that in the polymerization of isoprene with pentene-2, the more olefin present the lower the molecular weight of the polymers. This suggests that the pentene-2 is not interreacting with the isoprene, but is present in the role of mutual solvent. Even though pentene-2 and aluminum chloride form a complex, it is immaterial to the theory so long as a solution of the catalyst in the isoprene is obtained. If isoprene was treated with pentene–aluminum chloride complex, and never allowed to be in contact with the solid catalyst, then there should be obtained a minimum of insoluble polymers and a maximum of soluble polymers.

One mole of pentene-2 in 400 cc. of naphtha was stirred violently, while 40 g. of anhydrous aluminum chloride was added portionwise during two and one-half hours, at a temperature between 0 and 5°. Agitation was continued for an additional hour, when most of the aluminum chloride had reacted with the pentene-2; 1 mole of pure isoprene was added over a period of two and one-half hours. Much heat was evolved, and additional cooling was necessary to keep the mixture below 30°. The mixture was neutralized and finished in the usual manner. There was obtained 71.2 g. of soluble polymer and only 1.2 g. of the insoluble polymer.

Summary

1. In polymerization of isoprene by solid aluminum chloride, largely insoluble polymer is formed.

2. When the aluminum chloride is put into solution as a complex in the isoprene, largely a soluble polymer is produced.

3. Pentene-2 acts only as a "solubilizer" for the aluminum chloride when polymerized with isoprene, thus producing a low molecular weight or soluble polymer.

4. A theory for the above is suggested.

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[3] Houtz and Adkins, THIS JOURNAL, **55**, 1609 (1933).