

Relation between Denigés Reaction and Oxymercuration

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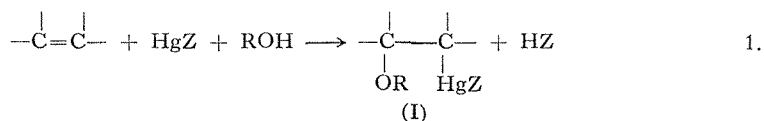
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Denigés reaction gives products entirely different from those of oxymercuration, despite that the reactants and the conditions of the both reactions are almost the same except that the former is applicable only to isoolefins usually and requires the presence of strong acid such as sulfuric or nitric acid. The relation of the two reactions has been studied, using isobutylene and mercuric perchlorate as the substrates. It is demonstrated that the oxymercuration product is formed primarily and reacts with mercuric perchlorate to form Denigés reaction product in the presence of perchloric acid. This explains the experimental facts that the products of the both reactions are formed in the reaction system above and the products ratio can be controlled by the reaction conditions. It is also demonstrated that Denigés reaction product can be converted to the oxymercuration product by the reaction with isobutylene under certain conditions.

1. INTRODUCTION

Denigés reaction is a well known test to detect isoolefin or *tert.* alcohol which can be dehydrated easily to form isoolefin in the presence of acid. Yellow precipitate is formed by introducing the substrate into the reagent which is prepared by dissolving mercuric oxide in aqueous strong acid such as sulfuric or nitric acid.¹⁾ Oxymercuration is a general reaction of olefin to form oxymercuration product (I) by the addition of mercuric salt in solvent ROH (R=H, alkyl and acyl) by equation 1.²⁾



While the reactants and the conditions of the two reactions are almost the same, except that the former is applicable only to isoolefins and requires the presence of strong acid, the products are entirely different. The former forms yellow precipitates and the latter gives clear solutions usually. In the literature, so far, no paper can be found to clarify the relation between the two reactions. This problem has been studied as a part of our program on the reaction of oxymercuration products with acid catalyst. As the strong acid, perchloric acid is used, since this has been used as the most convenient catalyst for various reactions of oxymercuration products.³⁾

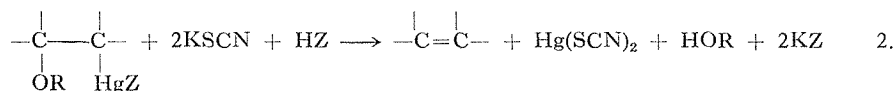
2. PRODUCTS OF THE REACTION OF ISOBUTYLENE WITH MERCURIC PERCHLORATE IN AQUEOUS PERCHLORIC ACID

Into the solutions which were prepared by dissolving mercuric oxide into 60% perchloric acid and then diluting with water, isobutylene was introduced without stirring

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at various temperatures. The resulting yellow precipitates (II) were filtered, washed with water, dried under vacuum for 24 hrs., and their mercury contents were determined by zinc dust-aqueous sodium hydroxide method.⁴⁾ The mercury contents were found to be $70.2 \pm 0.5\%$ and independent from the reaction conditions. Denigés gave a formula, $C_4H_8 \begin{smallmatrix} \text{HgNO}_3 \\ \text{HgHgNO}_3 \end{smallmatrix}$ (III), for the precipitate obtained in the presence of nitric acid. Substituting NO_3 in III with ClO_4 , the mercury content is calculated to be 70.24% and agrees with the experimental value obtained above. It is concluded, therefore, that the formula of II is $C_4H_8 \begin{smallmatrix} \text{HgClO}_4 \\ \text{HgHgClO}_4 \end{smallmatrix}$. When treated with concentrated hydrochloric acid at the temperature of steam bath, evolution of isobutylene from II was observed. No quantitative experiment, however, was carried out on this decomposition. By mechanical shock, II exploded violently.

The filtrates which were separated from II contained no inorganic mercury ions, because addition of aqueous sodium hydroxide did not form any precipitate. Addition of dilute hydrochloric acid (ca. 0.1 molar) to the filtrates resulted in evolution of isobutylene, and the resulting solutions formed yellow precipitate of mercuric oxide upon adding sodium hydroxide. The filtrates reacted also with potassium thiocyanate solution, despite that Hg^{++} was absent. All these observations show that the filtrates contain the oxymercuration product, 2-hydroxy-2-methyl-propyl-mercuric perchlorate. In a previous paper, it was demonstrated that the analysis of the oxymercuration products can be made by thiocyanate method according to equation 2.⁵⁾



By this method, the contents of I in the filtrates were determined. The total amounts of mercury (I + II) agreed with those of the starting mercuric oxide within experimental errors, except for the cases with perchloric acid concentrations higher than 2 molar at 26° and at 46° . At higher concentrations of acid and temperatures, formation of mercurous salt was observed.

It is concluded, therefore, that the products of the reaction of isobutylene with mercuric perchlorate are the oxymercuration product I and Denigés reaction product II, except for the cases with higher acid concentration and temperature.

3 EFFECTS OF THE REACTION CONDITIONS ON THE RATIO OF I TO II

The ratio of I to II in the product is affected by various conditions such as the amounts of isobutylene introduced (Fig. 1), the feed rates of isobutylene (Fig. 2), the concentrations of perchloric acid (Fig. 3), and the reaction temperatures (Fig. 4). These factors are not independent, but related each other. All these results appear to show that I is formed as the primary product of the reaction and then reacts further with mercuric perchlorate to form II in the presence of perchloric acid.

When insufficient amounts of isobutylene are introduced, I reacts with the unreacted mercuric perchlorate to form II, with the results that the larger the amounts of

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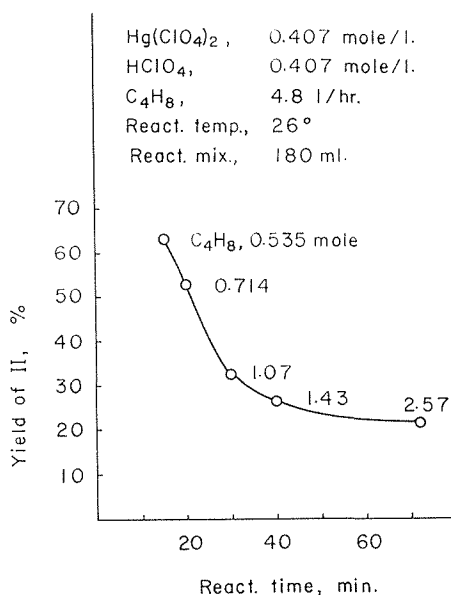


Fig. 1. Relationship between yields of II and the amounts of isobutylene introduced.

isobutylene introduced, the lower the yields of II become (Fig. 1).

The following experiment shows further that this assumption is correct. A solution (IV), which was prepared by dissolving 0.0734 mole of mercuric oxide in 39.3 g. of 60% perchloric acid and then diluting with water to 180 ml., was divided into two portions. Into one portion, isobutylene was introduced at a rate of 3.9 l/hr. for 40 mins. and the resulting mixture was filtered to remove II (0.0057 g. atom Hg). As was mentioned already, the filtrate contained I as the sole mercury compound (0.0310 g. atom Hg). Addition of the other portion of IV to the filtrate above resulted in formation of an additional amount of II (0.0468 g. atom Hg) after standing overnight at room temperature.

Even when sufficient amounts of isobutylene were added, the ratio of I to II depends on its feed rates. If the rate of reaction of I with mercuric perchlorate is comparable or slower, as compared with that of oxymercuration, the larger the feed rate, the smaller the concentration of free mercuric perchlorate becomes. Therefore, the ratio of II to I decreases with the increase of the feed rate (Fig. 2).

The increase of perchloric acid concentration appears to increase the rate of the second step to give the results shown in Fig. 3. At higher temperature of 46° , however, a maximum yield of II is observed. This indicates that a reverse reaction, $\text{II} + \text{isobutylene} \rightarrow \text{I}$, can proceed at higher concentration of perchloric acid and at higher temperature. It is demonstrated experimentally later that this is the case.

Increase of the reaction temperature resulted in the increase of the yield of II, presumably because of the increase of the rate of the second step.

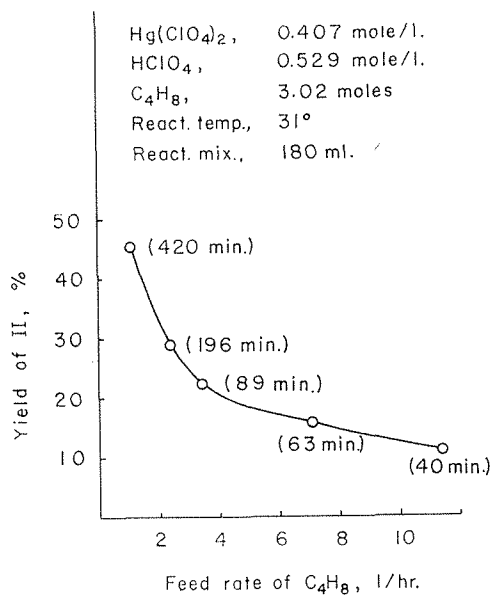


Fig. 2. Effects of isobutylene feed rates on yields of II

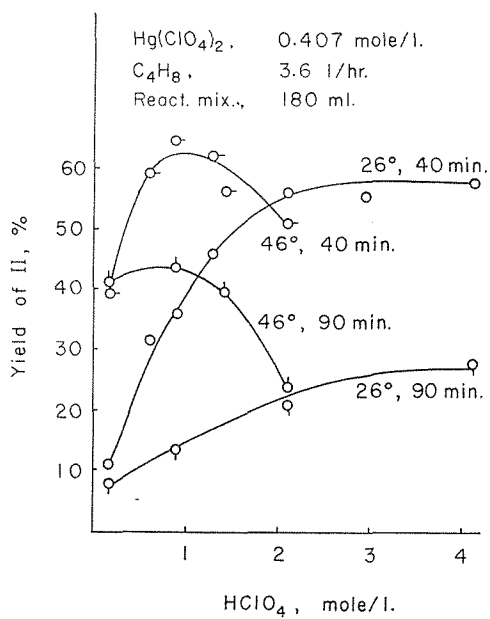


Fig. 3. Effects of perchloric acid concentrations on yields of II.

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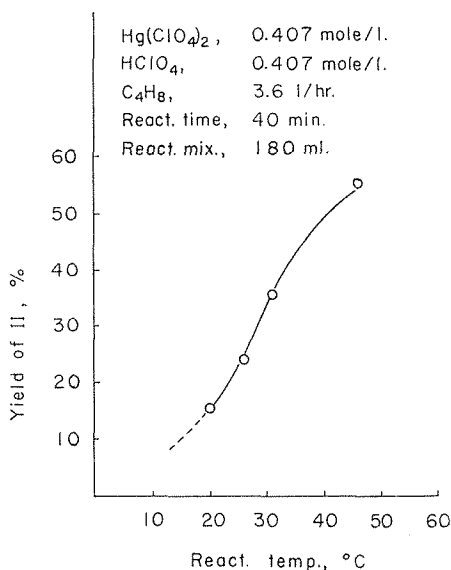


Fig. 4. Effects of reaction temperatures on yields of II.

4. FORMATION OF I FROM II IN THE PRESENCE OF ISOBUTYLENE AND PERCHLORIC ACID

A quantity of 0.0205 mole of II was added to 160 ml. of 1.38 molar perchloric acid. At 31° and under stirring, isobutylene at a rate of 3 l/hr. was introduced into this solution for 90 mins. After removing unchanged II, the filtrate was analyzed by both zinc dust-sodium hydroxide method and direct potassium thiocyanate method to show that it contained 0.0173 and 0.0168 mole of I respectively. It is clear, therefore, that II can be converted to I under certain conditions. The results at 46° shown in Fig. 3 appear to show that this reverse reaction becomes appreciable at higher concentration of perchloric acid and at higher temperature. However, under these drastic conditions, complicated reactions such as formation of mercurous salt and metallic mercury occur concurrently.

5. CONCLUSION

The experimental results and discussion described above show that the reaction of isobutylene with mercuric perchlorate in aqueous perchloric acid forms oxymercuration product and Denigés reaction product. The former is the primary product and reacts with mercuric perchlorate further to form the latter in the presence of perchloric acid. The ratio of the two compounds changes with the reaction conditions. Under certain conditions, the reverse reaction, Denigés-type precipitate + isobutylene → oxymercurial, proceeds, particularly at higher perchloric acid concentration and at higher temperature.

EXPERIMENTAL

Procedure. Into 60% perchloric acid, mercuric oxide was dissolved and diluted with water to make solutions of necessary concentrations of mercuric perchlorate and perchloric acid. Into this solution, isobutylene at constant rates was introduced without stirring. The yellow precipitate was filtered, washed with water and dried under vacuum for 24 hrs. to give dry samples of II. About 0.3 g. out of these samples was added to a mixture of 10 g. of sodium hydroxide, 2 g. of zinc dust, and 50 ml. of water and refluxed for 2 hrs. The zinc amalgam formed was washed with water by decantation several times and dissolved in 10 ml. of concentrated nitric acid. The solution was diluted with 100 ml. of water, added with a few drops of potassium permanganate (1 *N*) and then added with hydrogen peroxide to decolorize the solution. The resulting solution was analyzed with potassium thiocyanate (0.1 *N*). Mercury contents of all samples of II were $70.2 \pm 0.5\%$. The filtrate, which was obtained by filtering II off, formed no precipitate of mercuric oxide upon adding sodium hydroxide solution and was analyzed for the oxymercurial by direct thiocyanate method. Examples of data for mercury balance are shown below.

Table 1. Examples of mercury balance data.
Hg (ClO₄)₂, 0.407 *M*; C₄H₈, 3.6 l/hr.; react. time, 90 mins.; react. mix., 180 ml..

Hg used in starting system (A)	React. temp.	Conc. of HClO ₄	Hg in the products				B/A
			Hg in I		Hg in II		
g. atom	°C.	<i>M</i>	Zn dust method g. atom	KSCN method g. atom	Zn dust method g. atom	I + II (B) ^{b)} g. atom	
0.0734	26	0.81	0.0635	0.0632	0.0099	0.0731	1.00
		2.03	0.0560	0.0557	0.0174	0.0731	1.00
		4.07	0.0532	0.0514	0.0202	0.0716	0.98
	46	0.81	0.0415	0.0408	0.0319	0.0727	0.99
		1.35	0.0444	0.0436	0.0290	0.0726	0.99
		2.03	0.0580	— ^{a)}	0.0154	—	—

^{a)} Because of side reactions, this method of analysis was not applicable.

^{b)} Data by KSCN method were used for the calculation.

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