The Addition of Hydrogen Bromide to Undecenoic Acid in Toluene Solution. III. The Influence of the Impurities in Undecenoic Acid on the Effects of Oxygen and of Reduced Nickel.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received July 23, 1938.)

The addition of hydrogen bromide to pure undecenoic acid in toluene solution in the absence of air (oxygen) yields nearly pure 10-bromo-undecanoic acid.(1)(2) The presence of air (oxygen)(1) or reduced nickel(2) gives rise to the formation of more or less 11-bromo-undecanoic acid. The smaller the concentration of undecenoic acid in toluene solution, the greater the effect of either oxygen or reduced nickel.(2)(3)

Antioxidants, such as diphenylamine, catechol and hydroquinone, eliminate to a greater or smaller extent the effects of oxygen and of reduced nickel on the addition of hydrogen bromide to undecenoic acid in toluene solution.(4) These substances are more effective in inhibiting the action of oxygen than of reduced nickel, and diphenylamine has practically no influence on reduced nickel.(4)

Ashton and Smith(1) observed, in the addition of hydrogen bromide to undecenoic acid in ligroin solution, that the impurities, originated from

---

(1) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331.

(3) Similar observations were made by Ashton and Smith in benzene solution in presence of air.

(4) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 404.

the by-products in the preparation of undecenoic acid from ricinus oil, increased greatly the sensitiveness of undecenoic acid to oxygen, and as the impurities were removed, the undecenoic acid became less sensitive to oxygen.

In the present paper the authors deal with the influence of the impurities on the effects of oxygen and of reduced nickel in the addition of hydrogen bromide to undecenoic acid in toluene solution.

As the pure specimen of undecenoic acid a commercial product melting at 23.3–23.8° (corr.) (Kahlbaum, "extra pure") was used. The other specimen was prepared from ricinus oil and purified until it showed a melting point 20.5–21.7° (corr.). While the former was free from any traces of peroxides, the latter gave a very faint colouration with ammonium thiocyanate and ferrous ammonium sulphate. Even immediately after distilled in vacuum, the impure acid showed a slight peroxide reaction. Such a liability to form peroxides is a feature of impure undecenoic acid, and is caused probably by the presence of some aldehydes.(5) To protect the impure undecenoic acid, and even the pure if once its container was opened, from the formation of peroxides, they were kept in solid state in a refrigerator until use.

Hydrogen bromide was prepared by the action of bromine on hot tetralin and purified according to the directions of A. Klemenc.(6) Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen.

The results of experiments are shown in Tables 1 and 2. Hydrogen bromide was passed into the solution of 1.3 g. undecenoic acid in 20 c.c. toluene (more dilute than in the previous experiments) at 0°C. in the dark for an hour. The fundamental procedure of the experiments was the same as described in the first paper.(2) Thus, the additions in vacuum and in the presence of air and of reduced nickel were carried out just in the same manner as done previously. The reactions with the admission of given amounts of oxygen were carried out in the same way as the reactions in vacuum, except that, just before the introduction of hydrogen bromide, the required volumes of oxygen were admitted and the reaction vessels were shaken for five minutes.

The reaction mixtures were treated in the same way as before, and the compositions of the products were determined by measuring the melting (clearing) points (compare Fig. 2 of the first paper). Although the reaction was always complete, the impurities in the starting material

---

(5) Compare Ashton and Smith, *J. Chem. Soc.*, **1934**, 436.

(6) A. Klemenc, "Die Behandlung und Reindarstellung von Gasen," 196, Leipzig (1938).

Table 1. Pure undecenoic acid, m.p. 23.3-23.8°.

Exp. No.	In presence of	Product	
		Melting point (°C.)	11-Bromo-undecanoic acid (%)
1	None (vacuum)	34.6	2
2	Oxygen 0.5 c.c.	30.2	19
3	,, ,,	30.6	17
4	,, 1 c.c.	30.0	19
5	,, ,,	29.8	20
6*	Air	48.7	97
7	Reduced nickel 3.0 g.	25.5	34

* Exp. 5 of the first paper (3.68 g. undecenoic acid in 20 c.c. toluene).

Table 2. Impure undecenoic acid, m.p. 20.5-21.7°.

Exp. No.	In presence of	Product	
		Melting point (°C.)	11-Bromo-undecanoic acid (%)
8	None (vacuum)	33.0	8−
9	Oxygen 0.5 c c.	43.4	76+
10	,, 1 c.c.	46.1	86+
11	Air	48.4	96+
12	Reduced nickel 3.0 g.	26.0	35−

might affect the melting points of the products. However, it can be considered that the impurities were removed when the crystallized products were pressed on porous plates. The numbers in the last column of Table 2 were obtained by assuming the products contained only the two bromo-undecanoic acids. The minus and plus signs indicate that the percentage of 11-bromo-undecanoic acid should be smaller and greater respectively if the impurities still contaminated the products and lowered their melting points.

In absence of air the pure undecenoic acid gave nearly pure 10-bromo-undecanoic acid (Exp. 1), while the impure starting acid a product containing perhaps a greater amount of 11-bromo-undecanoic acid (Exp. 8). No difference was found between the pure and the impure specimens in the reactions in air (Exps. 6 and 11), the amount of oxygen absorbed under the conditions of the experiments being sufficient for producing the maximum proportion of 11-bromo-undecanoic acid in either case. However, with the limited amounts of oxygen, a great difference was observed between the pure and the impure specimens of undecenoic acid: With 0.5 or 1 c.c. oxygen, only about 20 per cent of the products from the pure undecenoic acid was 11-bromo-undecanoic acid (Exps. 2, 3, 4, and 5), while the proportion cf 10- and 11-bromo-undecanoic acids was nearly reversed in the products from the impure starting acid (Exps. 9 and 10).

Thus, the impure undecenoic acid was found to be far more sensitive to oxygen than the pure acid in the addition of hydrogen bromide in toluene solution, although the greater sensitiveness of the impure acid remains to be explained chemically. A possible explanation may be that, as the impure acid is much more liable to form peroxides than the pure as mentioned above, the former might absorb oxygen (partly in the form of peroxides) more easily than the latter, and, therefore, more oxygen (a part regenerated from the peroxides by the action of hydrogen bromide) might be present in the impure acid than in the pure during the addition reaction. If so, the presence of more oxygen would be simply the cause of the apparent greater sensitiveness of the impure undecenoic acid to oxygen. Otherwise, the peroxides, if not decomposed by hydrogen bromide, might be more powerful than molecular oxygen in reversing the direction of addition of hydrogen bromide, although the molecular oxygen is more active than the peroxide from allyl bromide in the case of the addition cf hydrogen bromide to allyl bromide.(7) Further, it may be also suspected that the impurities might act as oxygen carriers during the reaction. At any rate, nothing more concrete can be mentioned for the present.

On the other hand, the effect of reduced nickel seems not to be influenced by the impurities (Exps. 7 and 12). Even if the difference existing between Exps. 1 and 8 were taken into consideration or the impurities in the starting acid were assumed to affect the melting point of the product, it could be safely mentioned at least that the effect of reduced nickel was not increased by the impurities, contrary to the effect of oxygen. This may suggest the different mechanisms for the catalytic actions of oxygen and of reduced nickel, although their effects are very similar as seen from the results of the reactions which take place in their presence.

The authors express their hearty thanks to the Imperial Academy of Japan for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(7) This Bulletin, **12** (1937), 138.