The Addition of Hydrogen Bromide to Undecenoic Acid in Toluene Solution. II. The Influence of Antioxidants on the Actions of Oxygen and Reduced Nickel.

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In the previous work of this series it was established that an effect similar to that of oxygen is exhibited by reduced nickel on the addition of hydrogen bromide to undecenoic acid in toluene solution.[1] Some of the results of the previous experiments are quoted in Table 1 for the sake of comparison. The present paper is concerned with a comparative investigation of the influence of antioxidants on the actions of oxygen (air) and reduced nickel. The results are given in Table 2.

Table 1.

Undecenoic acid (g.)	Toluene (c.c.)	In presence of	Product	
			Melting point (°C.)	11-Bromo-undecanoic acid (%)
3.68	20	None (vacuum)	34.7	1
3.68	20	Air	48.7	97
2.5	20	Reduced nickel 3.0 g.	25.5	34

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Table 2.

Undecenoic acid 2.5 g. Toluene 20 c.c. Hydrogen bromide passed for one hour at 0°C. in the dark.

Exp.	In presence of	Product	
		Melting Point (°C.)	11-Bromo-undecanoic acid (%)
1	Diphenylamine 0.5 g. (22 mol %) Air	40.0	65
2	Diphenylamine 0.5 g. Reduced nickel 3.0 g.	26.5	31
3	Catechol 0.3 g. (22 mol %) Air	33.5	6
4	Catechol 0.3 g. Reduced nickel 0.3 g.	33.0	8
5	Hydroquinone 0.3 g. (22 mol %) Air	34.2	3
6	Hydroquinone 0.3 g. Reduced nickel 3.0 g.	32.6	10

Hydrogen bromide was passed for one hour at 0°C. in the dark into the toluene solution of pure undecenoic acid (2.5 g.) in the presence of an antioxidant (22 mol% to the acid) and either air (Exp. 1, 3, and 5) or reduced nickel (3.0 g.) (Exp. 2, 4, and 6). Diphenylamine (Exp. 1 and 2), catechol (Exp. 3 and 4), and hydroquinone (Exp. 5 and 6) were used as antioxidants. The antioxidants were dissolved in toluene together with undecenoic acid. Hydroquinone was sparingly soluble in toluene and mostly remained undissolved. In other respects the reactions were run in the same way as described in the previous paper.[1]

The reaction mixtures were treated also in the same way as previously. Diphenylamine (hydrobromide) remaining in white solid in the toluene solution was filtered off at 0°C. after hydrogen bromide was removed in vacuum. Catechol gave a reddish violet colour to the reaction mixture in presence of either reduced nickel or air. Catechol and hydroquinone were washed out with water until the washings gave no colouration with ferric chloride. The reaction was always complete and the products did not decolourize bromine. The composition was determined from the melting point as previously.

The inhibiting influence of diphenylamine on the action of oxygen was found rather weak (Exp. 1). This may be attributed at least partly to the effect of the solvent and especially to the small solubility of diphenylamine hydrobromide in toluene, because R. Ashton and J. C. Smith[2]

(2) *J. Chem. Soc.*, **1934**, 435.

observed a marked influence of diphenylamine on the action of oxygen in the addition of hydrogen bromide to undecenoic acid in ligroin solution. Diphenylamine exhibited a negligibly small influence on the action of reduced nickel (Exp. 2). In view of the weak influence of diphenylamine on the action of reduced nickel in the addition of hydrogen bromide to allyl bromide,[3] it can be supposed that, even if the diphenylamine salt were more soluble in toluene, the inhibiting influence on the action of reduced nickel would not be much stronger. Catechol and hydroquinone exerted a strong inhibiting influence on the actions of both oxygen and reduced nickel (Exp. 3–6). There may be found a certain parallelism between the case of allyl bromide[3] and that of undecenoic acid. In both cases, in the amounts used, reduced nickel exhibited a greater effect on the addition than oxygen in the present of any of the antioxidants so far used, while the order of the extents of their effects was reversed in absence of the antioxidants. In this sense it may be said that the antioxidants exerted a greater inhibiting influence on the action of oxygen than on that of reduced nickel, even though their actions can not be correlated to each other, oxygen being a homogeneous, and reduced nickel a heterogeneous, catalyst, and the mechanisms of their actions being quite obscure. Further it may be pointed out that in both cases (allyl bromide and undecenoic acid) the action of oxygen was inhibited the most severely by hydroquinone while that of reduced nickel by catechol.

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(3) See the preceding paper, this Bulletin, **13** (1938), 400.