J. Appl. Chem. USSR, 47, 2840-43 (1974)

INFLUENCE OF ISOSAFROLE AND OXYGEN CONCENTRATIONS ON THE DEGREE OF CONVERSION OF ISOSAFROLE INTO HELIOTROPIN

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UDC 547.538+541.15

We showed with reference to a number of examples [1] that when oxidation of alkenylbenzenes in acetic acid is initiated by ionizing radiation they are converted quantitatively in equl yields into the corresponding aromatic and aliphatic aldehydes, formed as the result of oxidation at the C=C bond in the side chain. This provides the possibility of obtaining a number of aromatic aldehydes, which are widely used in the food and perfumery industries [2, 3], by direct oxidation of the corresponding alkenylbenzenes with atmospheric oxygen. However, the aldehyde concentrations reach a limit at alkenylbenzene conversions in the region of 50% or higher [1]. We have attempted to find the factors determining the degree of oxidation of isosafrole to heliotropin in acetic acid solution at 23°, and to determine the compositions and yields of by-products in this process.

Limitation of the concentration of a particular product in the course of liquid-phase oxidation may be due to various causes: decrease of the concentrations of the original substances, self-retardation of the process long before the substance being oxidized is consumed completely, or, finally, subsequent conversions of the reaction product. In order to determine the relative roles which all these factors may play in chain oxidation of isosafrole, we studied the dependence of the limiting concentration of heliotropin on the initial concentration of isosafrole in solution and on the rate of passage of oxygen, and also the influence of additions of heliotropin on its limiting concentration.

Figure 1 shows kinetic curves for accumulation of heliotropin and consumption of isosafrole during oxidation of the latter in 1.1 M solution in acetic acid by oxygen bubbled at 240 and 60 ml/ml·h. It is seen from Fig. 1 that the limiting concentration of heliotropin increases with the oxygen feed rate. It is also easy to see that when almost 60% of the isosafrole has been consumed the rate of its oxidation is the same as at the start of the process, and is independent of the oxygen feed rate. At first sight it might be concluded from these data that the existence of a limiting concentration is due to oxidation of heliotropin into other products as it is formed. However, experiments on oxidation of heliotropin in acetic acid at 23° showed that its oxidation is slight at concentrations up to 0.5 M (solutions of higher concentrations were not investigated). Oxidation of isosafrole in presence of added heliotropin leads to the same conclusion. Figure 2 shows that the oxidation rate in presence of 0.37 mole of heliotropin per liter is the same as in absence of the additive, while the heliotropin concentration in solution increases linearly with the oxidation time, reaching a value 1.5 times the steady-state concentration during oxidation in absence of the additive. Therefore even if any heliotropin is consumed during oxidation of isosafrole the amount is very small.

Figure 3 shows kinetic curves for accumulation of heliotropin and consumption of isosafrole during oxidation of a 2.0 M solution of the latter in acetic acid at an oxygen feed rate of 60 ml/ml·h. It is evident from a comparison of these data with the curves in Figs. 1 and 2 that if the initial isosafrole concentration is doubled the limiting heliotropin concentration is also doubled. Therefore the degree of oxidation to heliotropin is evidently determined mainly by the isosafrole concentration in solution, increasing with increase of the initial isosafrole concentration. It also follows from Fig. 3 that only trans-isosafrole undergoes oxidation in acetic acid solution. The concentrations of its cis isomer and of safrole (the main impurity in isosafrole [4]) remain virtually unchanged during oxidation.

L. Ya. Karpov Physicochemical Institute. Translated from Zhurnal Prikladnoi Khimii, Vol. 47, No. 12, pp. 2751-2755, December, 1974. Original article submitted February 28, 1972.

TABLE 1. Yields of Products (Calculated on Isosafrole) Formed by Oxidation of 1.1 M Solution of Isosafrole in Acetic Acid

Products	Taken		Obtained		Losses	
	g	mole %	g	mole %	g	mole %
Isosafrole	21.63	100	11.00	50.7	0.81	0.37
Heliotropin			8.85	44.0		
Isosafrole oxide			0.99	3.7		
Piperonylic acid			0.13	0.7		
Polyperoxide			0.70	0.7		
Acetic acid	106.01	100	89.07	83.5	16.94	16.5

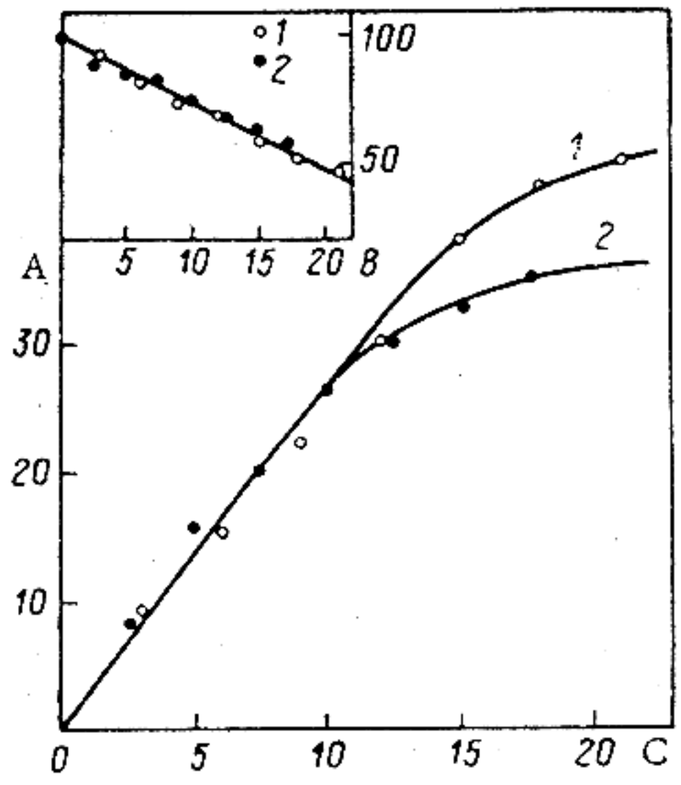

Fig. 1

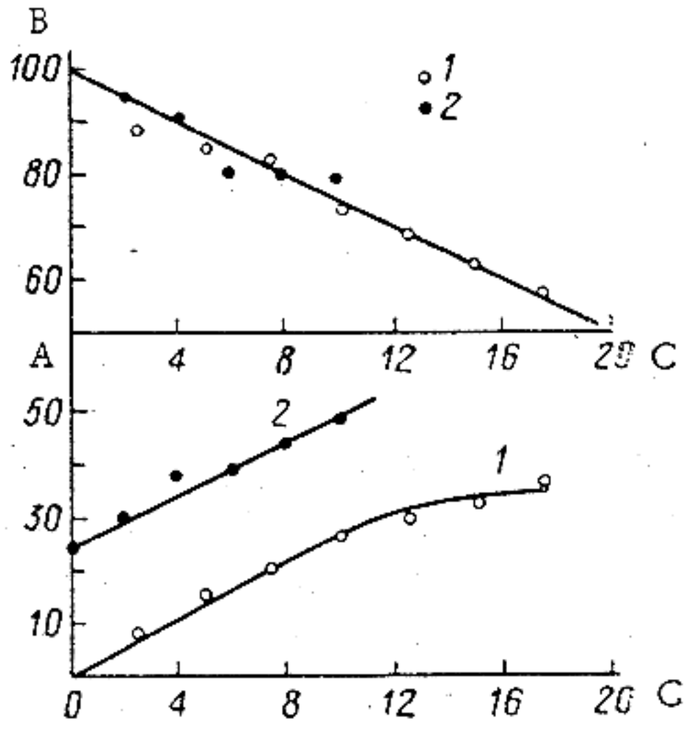

Fig. 2

Fig. 1. Accumulation of heliotropin and consumption of isosafrole during oxidation of the latter in 1.1 M solution in acetic acid by oxygen bubbled at 240 (1) and 60 (2) ml/ml·h. A) Amount of heliotropin (mole %); B) consumption of isosafrole (mole %); C) time (h); the same in Fig. 2.

Fig. 2. Accumulation of heliotropin and consumption of isosafrole during oxidation of the latter in 1.1 M solution in acetic acid. Oxygen passed at 60 ml/ml·h. 1) Without additive; 2) in presence of 0.37 mole of heliotropin per liter.

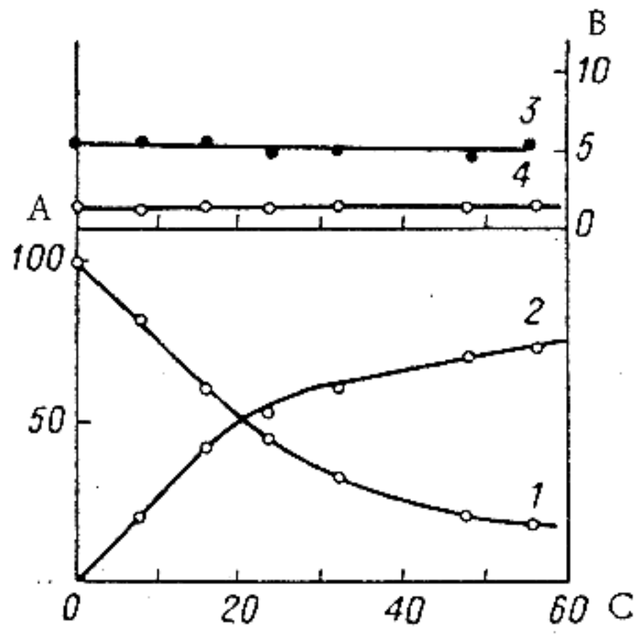

Fig. 3. Accumulation of heliotropin (2) and consumption of isosafrole (1) cis-isosafrole (3), and safrole (4) during oxidation of 2.0 M solution of isosafrole in acetic acid. A) Accumulation of heliotropin and consumption of isosafrole (mole %); B) consumption of cis-isosafrole and safrole (relative units); C) time (h).

Since the rate of isosafrole oxidation does not change when the limiting heliotropin concentration is reached, it is possible that a change of the oxidation mechanism occurs as the isosafrole becomes consumed, so that at the point when the limiting concentration of heliotropin is reached the composition of the reaction products may not be the same as at early stages of oxidation. To verify this hypothesis, we carried out a detailed study of the contents of polyperoxides, isosafrole oxide, aldehydes, and acids in oxidized isosafrole, isolating these products in the pure state. The results of one of these experiments are summarized in Table 1; they show that when the limiting concentration of heliotropin is reached the oxidation products also contain isosafrole oxide and polyperoxide, and piperonylic acid. It also follows from Table 1 that the difference between the rates of heliotropin formation and isosafrole consumption is due to oxida-

tion of isosafrole to isosafrole oxide and the polymeric peroxide. Piperonylic acid is, in all probability, formed by oxidation of heliotropin. Its yield suggests that the oxidation of heliotropin under these conditions is slight.

Thus, the hypothesis that the oxidation mechanism changes during consumption of isosafrole appears to be fully justified. Under such conditions it is quite natural that the heliotropin concentration should reach a limiting value, which depends on the initial isosafrole concentration, because under otherwise constant conditions oxidation by any particular mechanism must be determined by the concentration of the substance being oxidized.

EXPERIMENTAL

The oxidation, original substances, and methods of analysis of the products in kinetic experiments are described in the literature [4]. The oxygen concentration was varied by variation of the volume of isosafrole solution through which oxygen was bubbled at the rate of 7.2 liters/h. Initiation was effected by γ radiation; its intensity was $5.9\text{-}6.2 \cdot 10^{15}$ eV/ml · sec.

The UR-20 spectrophotometer was used for recording the IR spectra (of specimens in the form of tablets with KBr); the derivative thermograph devised by F. and J. Paulik and L. Erdey was used for differential thermal analysis.

The oxidation products were isolated and identified as follows. A solution of 21.63 g of isosafrole in 100 ml of glacial acetic acid was oxidized by oxygen, bubbled through at the rate of 60 ml/ml · h for 20 h. At the end of the oxidation the reaction mass (119.55 g) was left to stand in the dark overnight, and then filtered under reduced pressure to isolate isosafrole polyperoxide; yield 0.70 g, mp 113-114°. Differential thermal analysis showed that it decomposes exothermically in the 109-127° range with a sharp decrease of weight (by 60%). The melting point (exothermic peak) is 114°. At 380° a destructive endothermic reaction with evolution of gas occurs. IR spectrum (cm^{-1}): 1600, 1500 (aromatic ring); 1385 ($-CH_3$); 1200, 1045 ($-O-CH_2-O-$); 990 (aromatic $-O-O-$); 795 ($-CH_2-$). There are no literature data.

Found %: C 61.31, 61.60, H 5.51, 5.31.
$(C_{10}H_{10}O_4)_n$. Calculated %: C 61.86, H 5.15.

From the filtrate 89.07 g of acetic acid was isolated by recondensation* at 20° (12 mm), while the residue (28.35 g) was dissolved in 30 ml of toluene and treated twice with 20 ml of 5% sodium carbonate solution. The sodium carbonate extract was neutralized with sulfuric acid and extracted with ether; after removal of the solvent a gray substance was isolated; the yield was 0.133 g, mp 228.5° (from water). The literature value [5] is mp 228°. The IR spectrum of the substance was identical to the IR spectrum of piperonylic acid obtained by oxidation of perfumery-grade heliotropin with potassium permanganate in alkaline solution, and contained the following characteristic bands (cm^{-1}): 1680 (carbonyl C=O); 1625, 1504 (aromatic ring); 1418 ($-\overset{\overset{O}{\|}}{C}-O-$); 1300 (carboxyl OH); 1200, 1045 ($-O-CH_2-O-$); 790 ($-CH_2-$).

Found %: C 58.13, 58.10, H 3.91, 3.92.
$C_8H_6O_4$. Calculated %: C 57.80, H 3.70.

The residue after separation of piperonylic acid was treated twice, with stirring, with a twofold excess of 40% sodium bisulfite solution at 60° for 1 h, cooled to 20°, the bisulfite compound was separated off, and the organic layer was washed with distilled water to a neutral reaction and dried with anhydrous calcium chloride. After removal of toluene at 30° (37 mm) 11.99 g of isosafrole was obtained. Chromatographic analysis showed that it was enriched with the cis isomer and contained 8.5 wt. % of isosafrole oxide.

A solution of the bisulfite compound was put into a three-necked flask fitted with a mechanical stirrer, cooled in ice, and the calculated amount of 10% sodium carbonate solution was added dropwise with stirring during 1.5-2 h, care being taken that the temperature of the reaction mass did not exceed 5-7°. Filtration yielded 8.85 g of a white crystalline substance of mp 37-37.5° (from ethanol). According to literature data [5], mp 37°. Its IR spectrum was identical to the IR spectrum of heliotropin given in the literature [6], and contained the following characteristic bands (cm^{-1}): 2745, 2720 ($-CH=O$); 1616, 1504 (aromatic ring); 1250, 1045 ($-O-CH_2-O-$); 790 ($-CH_2-$).

Found %: C 64.20, 64.29, H 4.08, 4.15.
$C_8H_6O_3$. Calculated %: C 64.00, H 4.00.

*Recondensation is isolation of a more-volatile component from a mixture by vacuum evaporation followed by freezing with liquid nitrogen.

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