

Benzaldehyde oxidation test, a model reaction with radical mechanism. II.

The purification of benzaldehyde and stabilization of its activity

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A purification procedure for the preparation of benzaldehyde of convenient purity for the benzaldehyde oxidation test was worked out. Conditions on which the stable activity of the benzaldehyde stock is dependent were ascertained and a method for maintaining the stable activity elaborated. A procedure enabling to adjust the required activity of benzaldehyde in a narrow range was found and verified.

Разработан способ очистки бензальдегида, при помощи которого можно получить продукт чистоты необходимой для бензальдегидной окислительной пробы. Определены условия, от которых зависит постоянная активность рабочего запаса бензальдегида и разработан метод, обеспечивающий эту постоянную активность. Найден и проверен также способ, позволяющий установить требуемую активность от случая к случаю в узком интервале.

The only benzaldehyde suitable for the oxidation test must be chlorine free of anal. grade from which the active impurities were removed by repeated distillation at atmospheric pressure in a nitrogen atmosphere using a glass apparatus without lubricating the ground joints. To avoid leakage between ground joints and thereby the uncontrolled oxidation of benzaldehyde to benzoic acid which lowers the activity, it is recommended to put between the couple of ground joints a thin film of polytetrafluoroethylene. The benzaldehyde vapours condense in the ground joint and make it perfectly tight, moreover, the couple of joints could be well dismantled when cool. It is clear that traces of impurities, namely metals, influence markedly the benzaldehyde activity. The active impurities present in pure benzaldehyde or in that of anal. grade become visible after distillation leaving the distillation residue brown to yellow coloured. The criterion for the good quality of benzaldehyde is the colourless distillation residue.

Benzaldehyde prepared in this way has to be stored in bottles closed with cork stoppers from which the soluble substances were removed by successive extraction with benzaldehyde, toluene, ethanol, and water. The cork stopper contains about 2% of cork wax — cerine — and up to 1% a wealthy mixture of various substances as vanillin, tanning matters, dekacrylic acid *etc.* The dried cork stopper is impregnated with an aqueous solution of polyvinyl alcohol at reduced pressure and dried. As known, polyvinyl alcohol does not contain any inhibitors. Lubricated glass stoppers, rubber, polyethylene and polyvinyl chloride stoppers have to be avoided.

The stepwise lowering of errors increased the sensitivity of benzaldehyde to outer phenomena which, in turn resulted in the decreased reproducibility of oxidation of benzaldehyde itself. It has been found [1—4] that a perfectly pure and dried benzaldehyde in a dry flask in the dark did not undergo oxidation in the presence of oxygen. The weak autoxidation, which could be observed, is ascribed to the catalytical effect of the wall of the reaction flask. Basing upon these facts one could presume that the

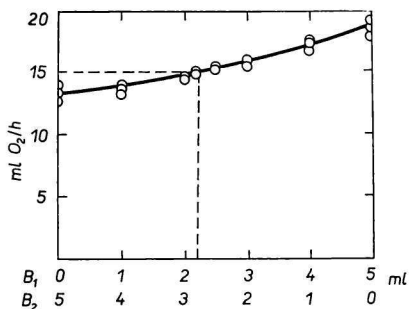


Fig. 1. Activities of mixtures of benzaldehydes.

The activities are expressed in ml O₂/h. B₁ is the stock in the smaller and B₂ in the larger bottle at hand. The required benzaldehyde activity is 15.0 ml O₂/h.

most important source of error was the unhomogeneous distribution of activated molecules of benzaldehyde throughout the vessel, in other words, the concentration of the activated molecules is greater near the walls than in the centre providing that the flask is not moved. This presumption was, however, to be experimentally proved.

Also the influence of the material of bottles on benzaldehyde was examined. Checked were: Sial, Unihost, Simax, brown bottle glass, Jena G-20, Jena Duran, polyethylene, polypropylene and coatings of polyvinyl alcohol and polytetrafluoroethylene. Benzaldehyde was stored in polyethylene and polypropylene bottles for some months before being purified, so that the degradation inhibitors were removed.

In order to make the benzaldehyde oxidation test a reliable method, the redistilled product had to be standardized. It has been found that its activity undergoes changes during the first 3—4 weeks and therefore the freshly distilled benzaldehyde should be stored 1—2 months in the dark at a constant temperature not exceeding 15°C. The standard activity of benzaldehyde could be achieved by continuous distribution of the activated molecules from the walls into the total volume by radial shaking. From several procedures tested, the most advantageous seemed to be to transmit pulses from an electric motor with a flywheel, the excentricity of which could be continuously adjusted by screws; thereby the pulse intensity was altered. The duration of the pulse and the relaxation time could be changed continuously by a timer.

The activity of benzaldehyde is strongly influenced not only by the alteration of the above-mentioned conditions, but also by the shape and the size of the bottle. Provided the level of benzaldehyde lies in the upper conical part of the bottle, the activity will be greater in a narrower bottle with a smaller volume than in that of greater diameter and volume at constant conditions. This fact could be utilized when preparing benzaldehyde of a given constant activity: Two bottles, *e.g.* 1.5 and 2.5 l were used for dynamic storage of benzaldehyde, both controlled by a common timer adjusted so that the activity in the smaller bottle will be greater than that in the larger one. By admixing both benzaldehydes in the proper ratio immediately before measurement, one can obtain the desired activity (Fig. 1). The bottle should be filled after consumption of approximately 0.5 l by benzaldehyde prepared a longer time before; the activity of the stock is then achieved within some days.

Experimental

The first distillation of benzaldehyde was carried out in a simple distillation apparatus at a temperature not exceeding 180°C, because at higher temperature a decomposition could take place and contaminate the distillate. The distillation residue contained *inter alia* benzoic acid. Redistillation was carried out in a column apparatus provided with a magnetic head, under constant flow of nitrogen in order not to influence the boiling point of benzaldehyde. The distillate was collected in a dark glass bottle under nitrogen from which it was poured into 0.5 l bottle with a screw closure packed with a teflon coated cork. After ageing at lowered temperature, benzaldehyde for oxidation test was withdrawn with a pipette through a centered, approximately 10 cm long glass tubing aiming to get benzaldehyde from the centre. The equilibration of benzaldehyde in the bottle standing on a polystyrene foam at a constant temperature was achieved after two days. The activity of the benzaldehyde withdrawn without any shaking was expressed in ml of O₂ consumed during one hour of oxidation at 20°C. The average consumption estimated was about 15 ml.

If benzaldehyde for oxidation was withdrawn near the wall of the bottle, the average consumption of oxygen was about 24 ml, if it was taken after vigorous shaking of the bottle the activity substantially dropped to 7 ml. This phenomenon could be due to more pronounced collisions of the activated molecules as in the preceding case; this resulted in the formation of adducts and in a decrease of activity.

The equilibration of activity of the benzaldehyde stock could be exemplified as follows: the volume of the bottle 1.5 l, the content of benzaldehyde 1.25 l, temperature within 14.6 to 15.2°C, the duration of the pulse 1.6 s, relaxation time 15.0 s, the motion residue of the motor 14 s. Under these conditions the activity of benzaldehyde was achieved in 20–22 days and the relative error was under 6%. A thorough withdrawal of benzaldehyde from the centre of the bottle was associated with a collapse of the activity equilibrium; the new equilibration takes about 1.5–2 hrs.

References

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