

Benzaldehyde oxidation test, a model reaction with radical mechanism. I. The method

J. GAŠPERÍK

*Department of Chemical Technology of Plastics and Fibers,
Slovak Technical University, 880 37 Bratislava*

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A sensitive method has been worked up which, being based upon kinetic measurements by means of a model reaction — oxidation of benzaldehyde in an oxygen atmosphere — enables to ascertain the concentration range in which the substance under study accelerates, retards, or inhibits the reaction proceeded by a radical mechanism. This method could be used to screen potential carcinogens, estimate the effectiveness of industrial catalysts, retarders and inhibitors and also to study the effect of various substituents from the theoretical point of view.

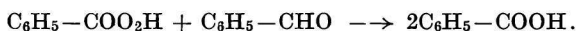
Был разработан чувствительный метод, который при помощи модельной реакции — окисление бензальдегида в атмосфере кислорода — дает возможность на основании кинетических измерений определить концентрационные области, в которых изучаемое вещество ускоряет, замедляет или ингибирует радикальные реакции. Этот метод можно использовать для скрининга потенциальных карциногенов, для определения эффективности промышленных катализаторов, ретардеров и ингибиторов, а также для теоретического изучения влияния различных заместителей.

A very important, nevertheless, hitherto little investigated and undervalued region is the influence of minimal concentration of various substances upon the course of reactions proceeding *via* radical mechanism. Recently evidence has been brought forward that some chemicals polluting the environment in quite low concentrations are involved in biochemical, for life inevitable radical reactions [1, 2]. The benzaldehyde oxidation test has been worked up on the basis of a model reaction used already for a longer time, the oxidation of benzaldehyde to benzoic acid. The old model reaction, to the contrary of this method, was associated with a great relative error.

The kinetics of the oxidation of benzaldehyde and the formation of reaction intermediates were studied by many authors. *Engler* and *Wild* found in 1897 [3] that the autoxidation of aldehydes proceeds through peroxide as intermediate. *Bayer* and *Villiger* [4] brought experimental evidence that peroxybenzoic acid is the oxidation intermediate. This problem was also investigated by *Staudinger* [5], *Almquist* and *Branch* [6]. *Bäckström* [7] proved that the light-initiated autoxidation of benzaldehyde is a chain radical reaction. *Reiff* [8] ascertained that a perfectly pure and dry benzaldehyde did not undergo oxidation in an oxygen atmosphere in a dry bottle in the dark; this finding was also reported by other authors [9—11]. A weak autoxidation was ascribed to the catalytical effect of the walls of the reaction vessel. Dif-

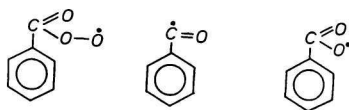
ferent results could be due to the fact that the oxidation of benzaldehyde is a chain radical reaction. The irreproducibility of results was explained by the presence of catalytically acting trace amounts of some metals [12, 13]. Although benzaldehyde was thoroughly purified by distillation, no reproducible results were obtained. *Mulcahy* and *Watt* [14] oxidized benzaldehyde of various proveniences before and after purification and obtained contradictory results. This indicates that the purification process removed either catalytically effective substances or oxidation inhibitors or retarders. *Almquist* and *Branch* [6] found the consumption of oxygen for autoxidation of benzaldehyde to be somewhat greater than that corresponding to the formation of peroxybenzoic and benzoic acids.

According to *Bayer* and *Villiger* [4] and *Brinner* and *de Chastoney* [15] peroxybenzoic acid oxidizes benzaldehyde without consumption of oxygen



Csürös, *Morgós*, and *Losonczy* [16] revealed new facts being in contradiction with the results of *Brinner* and *de Chastoney* [15] and *Brinner*, *de Chastoney*, and *Paillard* [17]. They investigated the autoxidation of benzaldehyde in the presence of various peroxides including peroxybenzoic acid and measured the consumption of oxygen, the peroxide content and identified the intermediates by means of infrared spectroscopy. Two of the peroxycompounds examined, namely di-*tert*-butyl peroxide and *tert*-butyl peroxide, accelerated the autoxidation at low concentration, whereas the reaction was retarded at higher concentrations and did not decrease under the oxidation rate of benzaldehyde itself. Peroxybenzoic acid and the dimer of cyclohexanone peroxide were unequivocally found to be inhibitors.

Spectroscopic study of this reaction argued against the presumption that peroxybenzoic acid was able to oxidize benzaldehyde without oxygen consumption. It has also been shown that peroxybenzoic acid underwent spontaneous decomposition, oxygen being the simultaneous catalyst and oxidation agent, or that peroxybenzoic acid acted as an oxygen transmitter. Dibenzoyl peroxide produced during the reaction could form three radicals, which are the reaction intermediates (Scheme 1).



Scheme 1

The autoxidation of benzaldehyde furnished a wealthy mixture of reaction products able to undergo mutual interactions. Because reactions with radical mechanism are involved, the linearity of the oxidation rate would depend on the satisfaction of the Bodenstein's rule — whether the number of free radicals formed in the reaction mixture within one time unit equals that of the extinguished radicals in the same time unit.

The principle of the benzaldehyde oxidation test lies in the determination of the oxidation rate of standard activity benzaldehyde in an oxygen atmosphere at constant conditions. It represents a micromethod sensitive to fractions of micrograms of the examined substance. Accurate results depend on the perfect purity and, therefore, it is recommended to clean flasks with *aqua regia* containing several crystals of

potassium iodide from which potassium periodate, decomposing organic substances, was formed. Sodium iodide could not be employed because sodium periodate flocculates in *aqua regia*. Neither chromosulfuric acid could be used, since traces of chemisorbed chromium containing substances influence the reaction course. More than 700 organic compounds were qualitatively tested in order to check the general use of this method. It has been shown that benzaldehyde is a good solvent of unpolar and a great deal of polar organic substances; every compound soluble at least partly in benzaldehyde influenced more or less its oxidation course.

Based upon quantitative measurements, substances could be classified into two groups: Compounds belonging to the first group accelerated the oxidation of benzaldehyde in certain low concentration range whilst the other did not accelerate the oxidation at all (Fig. 1), as exemplified by 5-nitrofurfuryl thiocyanate (active sub-

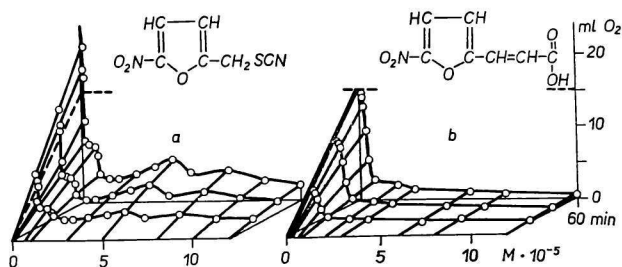


Fig. 1. Oxidation diagrams of 5-nitrofurfuryl thiocyanate (a) and 5-nitrofurylacrylic acid (b).

stance) and 5-nitrofurylacrylic acid. The amounts of the substance under study in mole $\cdot 10^{-5}$ per 5.0 ml of benzaldehyde are plotted on abscissa, the consumption of oxygen in ml on coordinate and time in minutes on the axis z . An example showing the possibility to screen potential carcinogenic substances by this method [18] (Fig. 2) is given by benzopyrenes: 1,2-Benzopyrene is a very effective carcinogen, 4,5-benzopyrene is its inactive counterpart. The dashed line intersecting the abscissa y shows the oxygen consumption of benzaldehyde without addition of any substance.

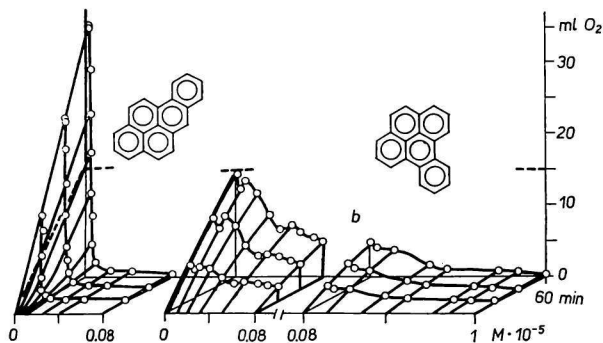


Fig. 2. Oxidation diagrams of 1,2-benzopyrene (a) and 4,5-benzopyrene (b).

The diagram shows the average value of 50–60 measurements with substances added within several orders of magnitude. Several maxima are seen in the low concentration range in which the acceleration of oxidation took place. The diagrams are simplified in order to be easy to survey and only peaks with the highest value were traced in the low concentration range. This method has been found to be suitable to compare the effect of inhibitors and retarders of radical reactions, to ascertain the activity of industrial catalysts and also to study the influence of various substituents from the theoretical view.

Experimental

The apparatus for the benzaldehyde oxidation test (Fig. 3) consists of a cylindrical reaction vessel with glass tubing provided with a stopper and an automatic electrolyzer kept at a constant temperature. The electrodes (1) are centrally located, the anode

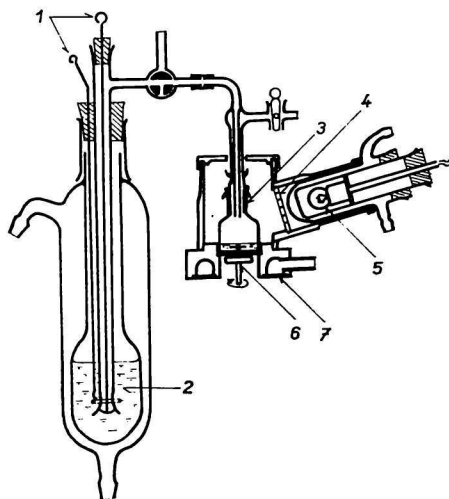


Fig. 3. Apparatus for oxidation test.

(Pt, \varnothing 1 mm) goes through the centre of the oxygen outlet, the ring-shaped cathode is made of 2 mm iron or stainless steel wire. The electrolyte (2) is an aqueous 5–6% potassium hydroxide solution, since no ozone is produced in it. The oxygen outlet is connected with a 3-way stopper serving for washing or filling the reaction vessel with oxygen from a gasometer. The automatic electrolyzer is very sensitive to changes of 0.02 to 0.05 ml in a closed apparatus. The reaction vessel (3) is placed in a light-tight white painted shield of an illumination block kept at constant temperature. The space between the container and the mantle filled with water forms a lens focusing beams coming from the light source (5) (an artificially aged 6 V, 5 W electric bulb underpowered to 5 V) through a green photofilter G.R.I. (4). The light intensity of every replaced bulb must be adjusted by means of a silicium photodiode located in the centre of the reaction vessel in the level of the reaction mixture opposite to the oncoming light. The bulb is fed by a stabilized electric source. The massive, constant temperature maintaining block is made of bronze. An electric motor, the rotating axle of which is provided with a permanent magnet (6) is adjusted closely to the block. Water from the ultrathermostat

flows through a ring-shaped canal (7) and keeps also the illumination device at a constant temperature. The reaction flask is placed in a 5 mm deep cut-out in the block filled with water to insure good heat transfer. At the 10 cm² face of the cylindrical flask the level of the benzaldehyde used (5.0 ml) is in 5 mm height. The integration mW-meter provided with a ml O₂ scale serves for recording the power supply for electrolysis.

Results of 40–60 measurements taken with substances at a 10⁻⁵ to 10⁻¹⁰ mole concentration per one mole of benzaldehyde are shown in a diagram in which the reaction course is expressed by consumption of oxygen. The ground joints of the apparatus are lubricated with silicon oil; it must be thoroughly removed after each measurement by washing with toluene, ethanol, water and immersed in *aqua regia* for at least 24 hrs.

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