

The Initiation Properties of 2-Cyano-2-propyl Hydroperoxide in Oxidation Processes

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The initiating ability of 2-cyano-2-propyl hydroperoxide in the oxidation reaction of cumene by molecular oxygen has been investigated and compared with the initiating ability of cumene hydroperoxide.

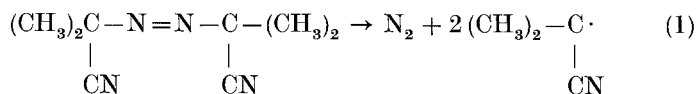
(Keywords: Autoxidation; Cumene; Initiation ability; Reaction rate of autoxidation)

Die Initiierungseigenschaften von 2-Cyano-2-propyl-hydroperoxid bei Oxydationsprozessen

Es wurde die Initiierungsfähigkeit des 2-Cyan-2-hydroperoxypropans in der Oxidation von Cumol mit molekularem Sauerstoff untersucht und mit der Initiierungsfähigkeit des Cumolhydroperoxids verglichen.

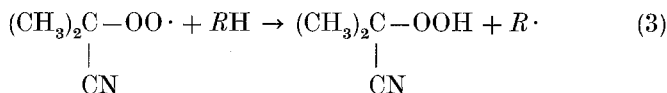
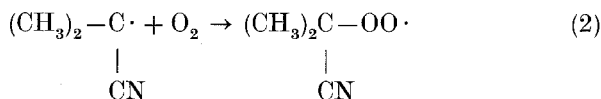
Introduction

Azobisisobutyronitrile (**1**) is one of the most important initiators used in the oxidation of organic compounds in liquid phase by molecular oxygen. This compound decomposes into free radicals by the following reaction:



*Bulygin*¹ found that the free radicals formed are oxidized to 2-cyano-2-

propyl hydroperoxide (**2**):



The hydroperoxide formed in this reaction may influence the oxidation reaction being itself initiator of radical chain reactions. **2** has been identified in the products of oxidation of ethylbenzene in the presence of **1**²⁻⁴. In the present paper the initiation properties of **2** in oxidation reactions have been investigated. The research was concerned with the kinetics of the autoxidation of cumene at 90–115 °C, and at a concentration of **2** of 0.1 mol dm⁻³. To obtain more detailed kinetic data at 110 °C, the concentration at this temperature has been varied from 0.08 to 0.1 mol dm⁻³. The initial rates of oxidation of mixtures of cumene with **2** were determined. For comparison the kinetics of cumene oxidation in the presence of cumene hydroperoxide was studied as well.

Experimental

Apparatus and Measurement Conditions

The oxidation reaction has been carried out in a gasometric apparatus⁵, the fundamental element of which was a 4 cm³ quartz flask, the flask was filled with mixtures of cumene and hydroperoxides. The total quantity of oxygen reacted was measured. The initial reaction rates were determined.

Reagents

Cumene: The technical cumene produced by Masovian Refineries (Mazowieckie Zakłady Rafineryjne i Petrochemiczne) in Płock was used. The technical product was purified according to a method described previously⁵. The purified product had the following characteristics: b.p. 40°/11 mm Hg, n_D^{20} 1.4920. Immediately prior to use the cumene was filtered through a 10 cm layer of neutral chromatographic aluminium oxide roasted at 350°. Filtration and filling of the flask were carried out in a nitrogen atmosphere.

2-Cyano-2-propyl hydroperoxide (2) was obtained according to a method described by *Dulog*³: b.p. 41°/0.25 mm Hg.

Iodometric analysis: Active O calcd.: 15.82%, found: 15.77%.

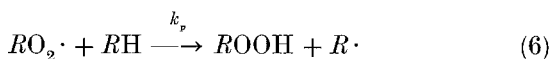
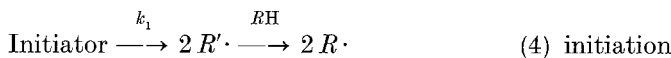
Azobisisobutyronitrile (1), technical product (Z. Ch. Bydgoszcz) was recrystallized several times from methanol, m.p. 103.5–104.0° (decomp.).

1,1-Azobis-1-cyclohexanenitrile (3). The method of *Overberger*⁶ for preparation and purification was used. M.p. 114.5–115.5°.

Cumene hydroperoxide (4) was obtained by cumene oxidation. The product was separated and purified as described in ⁵. B.p. 58°/0.2 mm Hg, n_D^{20} 1.5240. Iodometric analysis: Active O calcd.: 10.51%, found: 10.45%.

Results and Discussion

The oxidation reaction of hydrocarbons in liquid phase by molecular oxygen is a free radical chain process which may be described by the following reaction scheme:



where $R' \cdot$ —free radicals formed by decomposition of the initiator, RH —hydrocarbon.

Applying the usual steady-state assumptions, from which it follows that the rate of chain initiation r_i equals the rate of chain termination and that the rate of reaction (5) is equal to the rate of reaction (6) one obtains the following expression for the overall rate of oxidation

$$-\frac{dO_2}{dt} = -\frac{dRH}{dt} = \frac{dROOH}{dt} = \frac{k_p RH r_i^{1/2}}{k_t^{1/2}} \quad (8)$$

which is valid for long chain lengths; k_p and k_t are the rate-controlling propagation and termination rate constants. For the first order kinetics of hydroperoxide decomposition:



the rate of oxidation reaction r_{ox} is:

$$r_{ox} = k_i ROOH^{1/2} \frac{k_p}{k_t^{1/2}} RH \quad (10)$$

Table 1. Values of $\frac{k_p}{\sqrt{k_t}}$ for cumene

Temp. °C	90	100	110	115
$\frac{k_p}{\sqrt{k_t}} 10^{-2}$ [s ^{-1/2} m ^{-1/2} dm ^{3/2}]	1.02	1.30	1.70	1.85

If the values for r_{ox} and $k_p k_t^{-1/2}$ are known (7), the constant k_i can be calculated. r_{ox} was determined experimentally in the gasometric apparatus. $k_p k_t^{-1/2}$ was determined in the gasometric apparatus by the initiator method in which the initial oxidation rates of the mixtures of cumene with added initiators **1** and **3** were measured. The obtained values for $k_p k_t^{-1/2}$ are listed in Table 1.

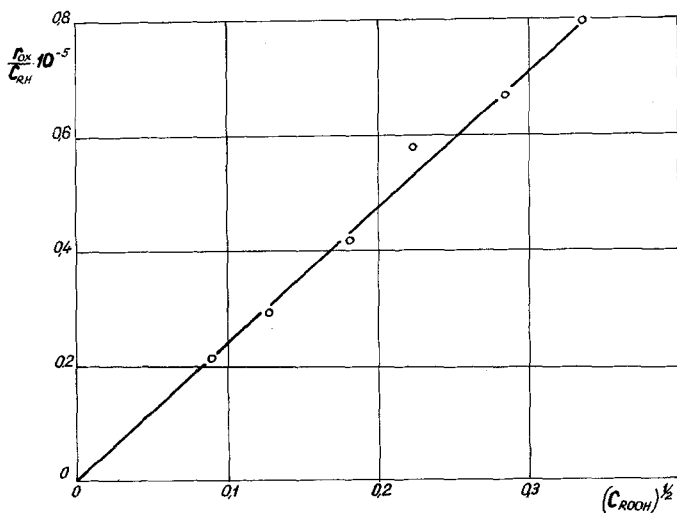


Fig. 1. Dependence of $\frac{r_{ox}}{RH}$ values on the hydroperoxide concentration

It was found that $\frac{r_{ox}}{RH}$ is proportional to $ROOH^{1/2}$ over the measured range of **2** concentration as is illustrated by Fig. 1. This confirms that the initiation process for this compound can be represented by first order kinetics.

Initiation capacities of **2** and **4** were compared and the results are listed in Table 2.

It has been shown that **2** is more active than **4**. The plot of $\log k_i$ versus $\frac{1}{T}$ shows a straight line and confirms therefore the *Arrhenius* temperature dependence of the reaction rate constant k_i . The values of k_i for **2** are much smaller than of k_i for **1**. Therefore the influence of **2** on the oxidation processes initiated by **1** is negligible.

Table 2. Oxidation of cumene with 2-cyano-2-propyl hydroperoxide and cumene hydroperoxide

Temp. °C	Cumene hydroperoxide			2-cyano-2-propyl hydroperoxide		
	Conc. of hydroperoxide [mol/dm ³]	$r_{ox} 10^{-5}$ [mol/dm ³ s]	$k_i 10^{-6}$ [s ⁻¹]	Conc. of hydroperoxide [mol/dm ³]	$r_{ox} 10^{-5}$ [mol/dm ³ s]	$k_i 10^{-6}$ [s ⁻¹]
90	0.100	0.971	0.2158	0.1045	1.70	0.661
100	0.100	1.700	0.405	0.1007	3.40	1.606
110	0.100	3.340	0.932	0.1100	5.08	1.987
115	0.100	5.400	2.120	0.1005	6.31	2.940

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