CONCLUSIONS

1. Rates of initiated joint oxidation in 52 binary R\textsuperscript{1}H--R\textsuperscript{2}H systems: n-paraffin-alcohol, n-paraffin-ester, ester-alcohol, alcohol-ether have been obtained from measurements of O\textsubscript{2} uptake at 403\textdegree{}K. The reactivity of R\textsuperscript{1}H relative to R\textsuperscript{2}O\textsuperscript{\bullet} has been estimated in those cases in which the rate of oxidation was increased by addition of the second component.

2. A multidipole effect appears in the reactions of polyfunctional alcohols and esters with peroxide radicals. The contribution of this effect to the Gibbs activation energy varies from 2.4 to 6.1 kJ/mole, depending on the structure. The activity of the peroxide radical also depends on the number and type of the functional groups in the molecule.

LITERATURE CITED


AMINOSULFIDE-CATALYZED DECOMPOSITION OF CUMENE HYDROPEROXIDE AND THE INHIBITING ACTION OF THE AMINOSULFIDE DECOMPOSITION PRODUCTS

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The products resulting from the reaction of hydroperoxides with phenol sulfide suppress the radical chain oxidation of hydrocarbons, effectively destroying the peroxide molecules and rupturing the oxidation chains in the hydrocarbon itself [1]. The ability of two different aminosulfides (AS) to destroy hydroperoxide molecules has been studied in the present work. A study has also been made of the ability of the products resulting from the interaction of one aminosulfide with cumene hydroperoxide (CHP) and tert-butyl hydroperoxide (TBHP) to react with peroxide radicals in the styrene oxidation.

EXPERIMENTAL

1-Anilino-2-mercapto- and 1-anilino-2-butylthio-3-butoxypropane, C\textsubscript{9}H\textsubscript{9}OCH\textsubscript{2}(SH)CH\textsubscript{2}NHC\textsubscript{6}H\textsubscript{5} (AMS), C\textsubscript{9}H\textsubscript{9}OCH\textsubscript{2}CH(SC\textsubscript{4}H\textsubscript{9})CH\textsubscript{2}NHC\textsubscript{6}H\textsubscript{5} (BAS), were synthesized by the methods of [2]. Their structures were confirmed by IR spectroscopy and their purities by liquid-gas chromatography [3]. The CHP was purified as the Na salt, and then distilled. The TBHP was subjected to two successive fractionations. The chlorobenzene and cumene were purified by sulfonating the reaction mixture with concentrated H\textsubscript{2}SO\textsubscript{4}, a standard procedure. The styrene was subjected to repeated fractionation under vacuum. Studies on CHP decomposition were carried out in chlorobenzene, working under an inert-gas atmosphere in a glass bubble reactor, analysis for the CHP content of the system being carried out by iodometric methods. The oxidation measurements were performed in the manometric system described earlier in [1]. The inhibiting action of the product resulting from the AMS-hydroperoxide interaction was studied in the solution left after complete breakdown of the CHP or TBHP, as the case might be. The concentration of this product was assumed equal to the original AMS concentration.

DISCUSSION OF RESULTS

Kinetically speaking, the breakdown of CHP under the action of AMS and BAS is a complex process, reaction being preceded by an induction period whose length varies with the working conditions, just as in the case of phenolsulfide. Decomposition sets in at the end of the induction period and proceeds, from then on, at a constant rate. At [AS] = const, this rate is proportional to [CHP]; at [CHP] = const it is proportional to the initial AS concentration (Fig. 1). Formally, the concentration dependence of the rate of CHP breakdown in the presence of either AS is given by an expression in the form \( W = k[\text{CHP}][\text{AS}] \), i.e., by the rate equation for a simple bimolecular process. Calculated from the temperature variation of \( k \) (Fig. 2), the activation energy proved to be \( 89.5 \pm 6 \) kJ/mole for AMS and \( 96 \pm 8 \) kJ/mole for BAS. Values of the length of the induction period and rates and rate constants calculated from the Arrhenius equation (\( \log k = 12.96-89.5/RT \) for AMS and \( \log k = 13.95-96/RT \) for BAS) are shown in Table 1. The fact that the activation energies and rate constants were essentially the same for AMS and BAS suggested that it is the same type of active particle which was responsible for the catalytic breakdown of CHP, regardless of whether it was AMS or BAS which was being oxidized by the hydroperoxide. This assumption was supported by Fig. 3 which shows \( \nu = \Delta[\text{CHP}]/[\text{AS}]_0 \) plotted against \([\text{CHP}]_0/[\text{AS}]_0 \) (\( \nu \) is the mean number of CHP molecules decomposed per AS molecule introduced into the system, or, more exactly, per molecule of product resulting from oxidation of AS by the hydroperoxide). The curves of this figure are coincident up to \([\text{AMS}] = [\text{BAS}] = 8\times10^{-4} \) mole/liter, and even their limiting values are not radically different. The catalytic effect was quite marked here, the maximum value of \( \nu \) being 35,000 for BAS and 44,000 for AMS.

Protection of hydrocarbons against oxidation requires not only effective measures for hydroperoxide destruction but also treatment leading to the suppression of radical oxidation processes. We found that chain reactions were inhibited by the products (PAS) resulting from the interaction of AS with CHP and TBHP. As much was indicated by the fact that the rate of initiated styrene oxidation proved to be dependent on the concentration of ASP introduced into the system (Fig. 4, curve 1). The fact that chain rupture was a linear process in the presence of ASP was indication that there is a proportional relation between the styrene oxidation rate and the concentration of the initiator, azocyclohexynitrile (ACHN). The inhibiting action of the product resulting from the reaction of CHP and AMS was similar to that of the product formed in the reaction of TBHP with AMS, equal concentrations of ASP (TBHP) and ASP (CHP) giving almost identical reductions in the rate of initiated styrene oxidation (white and black points on curve 1). The quantity \( 2k_\gamma/W_0/W \) [4] was evaluated by reploting the data of Fig. 4 in \( W_0/W - W/W_0 \) vs [PAS] coordinates, and then measuring the slope of the resulting straight line (curve 3); from the value so obtained and the value of \( k_\gamma \), namely, \( 8.5\times10^7 \) liters/mole·sec, taken from [5], it was found that \( k_\gamma = 2.04\times10^5 \) liters/mole·sec. The product resulting from the oxidation of AMS by hydroperoxides was therefore a much more active inhibitor than