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Abstract

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LOCAL ACTIVATION OF COMPOUNDS WITH A CONJUGATION SYSTEM IN REACTIONS INVOLVING THE INHIBITION OF OXIDATIVE PROCESSES*

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Earlier (1) it was shown that the effectiveness of hydrocarbons of the acene series as inhibitors of the thermal oxidation of paraffinic hydrocarbons is closely related to the ease with which they are excited into the biradical triplet state. In particular, it was established that anthracene, characterized by a comparatively high excitation energy, unlike naphthacene and pentacene, is a very ineffective inhibitor of paraffin oxidation at 160–200°. On the other hand, the presence in higher acenes (naphthacene, pentacene) of paramagnetic particles (p.m.p.) and the absence of an EPR signal for anthracene were established (A. A. Berlin, V. A. Vonsyatskii, L. S. Lyubchenko). It was suggested that this picture is due to the manifestation of the previously discovered (2,3) "local activation effect" of compounds with a system of conjugated bonds by p.m.p. formed during the synthesis or subsequent treatment of these compounds. Since the probability of singlet-triplet transitions in aromatic compounds increases under the influence of paramagnetic molecules (5,6), it was natural to assume that the activation products of anthracene containing p.m.p. would be significantly more effective acceptors of free radicals (and, consequently, inhibitors of chain radical processes) than the original anthracene. To test this assumption we investigated the dependence of the inhibiting activity of pro-

Table 1

Fraction	Fraction yield, %	Solubility in benzene	Solubility in methanol	Mol. wt. (avg.)	C/H ratio by elemental composition	p.m.p. content/g	Distance between maximum-slope points of EPR signal, oersted	Absorption bands in the UV and visible region, mμ
Anthracene	–	+	+	178	16.8	–	–	251, 323, 338, 354, 374
I	68	+	+	182	17	$8 \cdot 10^{16}$	7	In addition to anthracene bands, 420, 440, 463, 475, 503, 602
II	10.3	+	–	750	19	$2 \cdot 10^{18}$	5.5	Continuous background without characteristic bands in the region 240–620

Fig. 1 and Fig. 2 diagrams

Figure 1: Fig. 1 and Fig. 2 diagrams

Fraction	Fraction yield, %	Solubility in benzene	Solubility in methanol	Mol. wt. (avg.)	C/H ratio by elemental composition	p.m.p. content/g	Distance between maximum-slope points of EPR signal, oersted	Absorption bands in the UV and visible region, mμ
III*	19.8	–	–	–	23	$1\cdot10^{19}$	4.5	

* Fraction III is soluble in quinoline and pyridine.

* L. A. Mostovaya and N. V. Khruslova took part in the experimental part of the work.

products of varying degrees of anthracene activation on the content of p.m.c. in them. The increase in the p.m.c. content in the course of anthracene activation is shown in Fig. 1.

The EPR signal of the anthracene-activation products is a narrow singlet with the g-factor of a free electron, and its magnitude is the same in air and in vacuum and does not change during prolonged storage in air at room temperature. A correlation was then indeed established between the p.m.c. content in activated anthracene and its ability to inhibit the thermal oxidation of paraffins (cetane, ceresin*) (^{7}), and to interact with stable radicals (diphenylpicrylhydrazyl) and monomers (^{3,4}).

Fig. 1. Dependence of the p.m.c. content in anthracene activation products (1) and of the induction periods in the oxidation ($T = 160^\circ$) of ceresin (2) on the depth of activation. Inhibitor concentration 1 wt. %.

Fig. 2. Dependence of the induction periods in the oxidation of ceresin on the p.m.c. content in unfractionated anthracene activation products (1) and in artificial mixtures: fraction II + anthracene (2), fraction III + anthracene (3), and fraction II + fraction I (4). Total inhibitor concentration 5 wt. %, $T = 200^\circ$.

As can be seen from Fig. 1, there is an extremal dependence of the induction periods** in the oxidation of ceresin on the p.m.c. content in activated anthracene, the maximum of which corresponds to a concentration of $\sim 2\cdot10^{18}$ p.m.c./g

Figure 3 and Figure 4

Figure 2: Figure 3 and Figure 4

of inhibitor. A completely analogous dependence is observed when products of the activation of certain polymers with conjugated bonds (polyphenylacetylene) are used as oxidation inhibitors. The results obtained were interpreted from the standpoint of a lowering of the excitation energy of the principal mass of inhibitor molecules under the influence of paramagnetic polymer homologs present in the products of its activation. It appeared important to attempt to activate diamagnetic inhibitor molecules by individual paramagnetic fractions isolated from the products of its activation. The characteristics of three such fractions, isolated from anthracene activated to a content of $2 \cdot 10^{18}$ p.m.c./g, are presented in Table 1.

The influence of paramagnetic particles on the activation of anthracene was studied by using mixtures of fraction II + anthracene as inhibitors (Fig. 2). When fraction II was diluted with pure anthracene to a p.m.c. content corresponding to the points of curve 1 in Fig. 2 (within the same total—

* Purified *n*-paraffin, containing no unsaturation or aromatics and having, on average, less than 1 branch per molecule.

** The induction period was taken as the time from the start of the reaction until absorption of 0.1 ncm^3 O_2/g of the oxidized substrate.

···inhibitor concentration of 5 wt.%), effects analogous to those observed for the unfractionated products occur. Two features are characteristic of the dependence obtained. The first is the presence of a maximum on the curve, the position of which corresponds to the same content of paramagnetic particles as in the unfractionated product ($\sim 5 \cdot 10^{17}$ paramagnetic particles/g). The second is the smaller absolute values of the induction periods, as compared with the corresponding periods caused by the unfractionated products (at the same content of paramagnetic particles). It could be assumed that responsible for this discrepancy is the activation fraction III present in the unfractionated products.

Fig. 3. Dependence of the induction periods upon oxidation of ceresin on the concentration of anthracene in the absence (1) and in the presence (2) of 0.1 wt.% fraction II, $T = 160°$.

Fig. 4. Kinetics of oxidation of ceresin at 160°: 1 —pure ceresin; 2 —ceresin + 5 wt.% polyphenylene; 3 —ceresin + 5 wt.% polyphenylene + 0.1 wt.% fraction II; 4 —ceresin + 5 wt.% anthracene; 5 —ceresin + 5 wt.% anthracene + 0.1% fraction II.

However, curve 3 in Fig. 2 indicates a very weak inhibiting action exerted by fraction III when it is diluted with pure anthracene. This is probably connected with the insolubility of this fraction. On the other hand, when fraction II is diluted with fraction I, the values of the induction periods practically coincide with the induction periods caused by the unfractionated activation products containing the same number of paramagnetic particles. Thus, the products of anthracene condensation, present together with unreacted anthracene in fraction I and characterized by greater ease of excitation to the triplet state under the influence of paramagnetic particles, as compared with anthracene, are responsible for the difference in the induction periods. The dependences presented in Fig. 2 also hold at 160 and 180°. The presence of a maximum on curve 2 indicates that a decrease in the solubility of the products of deeper activation of anthracene is not the only factor determining the decrease in the effectiveness of their inhibiting action. Evidently, within the given inhibitor concentration there exists an optimal ratio between the number of paramagnetic particles and diamagnetic anthracene (or its higher-molecular condensation products), at which the maximum induction periods are realized. At a given concentration of the paramagnetic fraction, the induction periods increase sharply with an increase in the amount of anthracene introduced into the system (Fig. 3). This indicates the possibility of transferring the activating influence of paramagnetic particles to a large mass of molecules of the activated diamagnetic inhibitor. The results obtained lead to the fundamental conclusion that, for the inhibiting action of monomeric and polymeric compounds with a conjugation system to appear, under···

In thermal oxidation, the presence in the inhibitor of very small amounts of p.m.c.—centers of local activation (c.l.a.)(4,8)—is necessary. The p.m.c. arising in the products of activation of anthracene and other monomeric and polymeric compounds with a conjugation system (polyphenylacetylene, polyphenylene, etc.) as a result of quasiradical polymerization are stable block polymers, apparently of ion-radical nature(4). Owing to their ion-radical character, the c.l.a. are capable of polarizing the surrounding diamagnetic molecules of the inhibitor, facilitating excitation of the latter into the triplet state. In view of the foregoing, the activating influence of the c.l.a. should depend strongly on the "packing density" of the molecules being activated around these centers, since only in this case is sufficiently effective polarization possible. A consequence of this should be the high specificity of the activating action of the c.l.a. Indeed, activation occurs only when the chemical structures of the activator and of the compound being activated are close. Thus, paramagnetic fraction II, isolated from activated anthracene and very effectively activating anthracene, only slightly changes the reactivity of other polyconjugated systems (polyphenylene, polyphenylacetylene) (Fig. 4). In turn, these polymers, containing p.m.c., do not exert an activating influence on anthracene. Evidently, the concepts being developed regarding the influence of paramagnetic c.l.a. on the inhibiting activity of compounds with a conjugation system are of a general character, making it possible not only to explain the action of such systems in inhibition reactions, but also, possibly, to serve as a basis for understanding hitherto unexplained cases of synergism of certain organic antioxidants and carbon blacks(8).

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Note: Figure translations are in progress. See original paper for figures.