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Abstract

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Local Activation of Anthracene in the Course of Oxidation of Paraffins Inhibited by Tetracyanoethylene–Anthracene Mixtures

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It is known that the formation of charge-transfer complexes (CTCs) increases the probability of $S \to T$ transitions in compounds with a conjugated system (in particular, in aromatic hydrocarbons) (1). This circumstance should lead to an increase in the reactivity of the indicated compounds and, in particular, facilitate their conversion into paramagnetic polymeric products (2,3). Until recently, the question of the mechanism of the transition from formally valence-saturated monomeric compounds with a conjugated system (for example, polynuclear aromatic hydrocarbons) to paramagnetic polymers has still not been clear. However, there is reason to believe that these transformations are apparently associated with the ease with which these compounds form adducts and with the ability of the latter to undergo further conversion into polymeric substances. Taking into account that most compounds with a conjugated system have a relatively low ionization potential, it could be assumed that the increase in the reactivity of these compounds (and, in particular, anthracene) will be achieved to a greater extent the higher the electron affinity of the substances forming CTCs with them.

[Figure 1 and Figure 2: plots shown on the page]

Fig. 1. Dependences of the induction periods in the oxidation of kerosene (T 180°) on the concentration: of anthracene (1a) and TCE (2a); of anthracene in the absence (1b) and in the presence (2b) of 1 wt.% TCE; 3b –additive curve

Fig. 2. Dependences of τ_{ind} in the oxidation of kerosene (T 180°) on the weight fraction of TCE in its mixture with anthracene. Total inhibitor concentration 2 wt.% (1) and 3 wt.% (2)

One of the strongest electron acceptors is tetracyanoethylene (TCE)–a strong π-acid, characterized by an electron affinity value of 1.6 eV (4). TCE readily forms colored complexes with many aromatic hydrocarbons even upon simple mixing.

components (donor–acceptor) in a common solvent. In the case of anthracene, the green-colored complex formed upon its interaction with TCNE in benzene

Figure 3 graph

Figure 1: Figure 3 graph

Figure 4 graph

Figure 2: Figure 4 graph

solution rapidly changes into a white crystalline adduct owing to the addition of TCNE at the 9,10-positions of the anthracene molecule (4). On the basis of the recently established fact* of the formation of paramagnetic polymers in the interaction of TCNE with anthracene, and also on the basis of the phenomenon we established of activation of compounds with a conjugated system under the influence of paramagnetic polymer particles in reactions inhibiting oxidative processes (5), it seemed interesting to investigate the inhibiting activity of various combinations of anthracene with TCNE in the oxidation of paraffin hydrocarbons.

Fig. 3. Dependence of the induction periods during oxidation of ceresin (T 180°) on the concentration of anthracene in the absence (1) and in the presence of 1 wt.%, 2.5 wt.% and 5 wt.% of the TCNE—anthracene adduct (2, 3 and 4, respectively)

Fig. 4. Kinetics of accumulation of paramagnetic particles in the inhibitor during oxidation of ceresin with 5% equimolar TCNE—anthracene mixture at 180°. 1 —in air; 2 —in nitrogen

As can be seen from Fig. 1, TCNE itself possesses a slight inhibiting activity, which is consistent with its ability to add free radicals (4). In the presence of 1 wt.% TCNE, the induction periods during oxidation of ceresin increase sharply with the introduction into the system of increasing amounts of anthracene, and these effects exceed additive ones by more than an order of magnitude. Within the limits of the given total inhibitor concentration, the maximum induction periods occur at an equimolar TCNE—anthracene ratio, i.e., at the ratio corresponding to adduct formation (Fig. 2). Additions of the preformed adduct activate anthracene, sharply increasing the induction periods caused by the latter (Fig. 3).

Thus, the observed effects of anthracene activation are analogous to those that occur when paramagnetic fractions isolated from the products of heat treatment of anthracene or polyphenylacetylene are used as activating additives to anthracene (3).

Taking into account the considerations presented above on the activating role of charge-transfer complexes in the formation of paramagnetic polymers, it was of interest to verify whether the activation effects observed in the inhibition of oxidation by TCNE—anthracene mixtures are associated with the emergence of paramagnetic polymers during the course of oxidation. For this purpose, the oxi-

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of ceresin in the presence of additions of TCNE—anthracene mixtures directly in the resonator of the EPR spectrometer. In the course of oxidation, the appearance of a stable EPR signal does indeed occur already in the first minutes of heating at 180°, with the signal intensity rapidly increasing to a value corresponding to $\sim 10^{18}$ paramagnetic particles (p.m.p.) per gram of inhibitor and then no longer changing (Fig. 4). The form of the EPR signal is a narrow singlet with the g-factor of a free electron, i.e., it is analogous to the EPR signals known for other polyconjugated systems. The same picture was also observed when oxidation was inhibited by the prepared TCNE—anthracene adduct. When oxidation was inhibited by anthracene, no EPR signal was detected (the initial TCNE and the TCNE—anthracene adduct do not give an EPR signal). Analogous experiments carried out in an atmosphere of N_2 showed that, although the appearance and growth of the EPR signal intensity also occur under these conditions, the maximum value reached by the signal is considerably (by more than an order of magnitude) smaller than in the presence of oxygen. This indicates the essential role of $RO_2^\bullet$ radicals in the mechanism of formation of paramagnetic particles.

At present there is not yet a sufficient amount of experimental data to make it possible to interpret this mechanism unambiguously. However, the role of adduct formation and their decomposition at higher temperatures is beyond doubt, as is the influence on this process of dehydrogenating agents (in the case considered, $RO_2^\bullet$ radicals). In this connection it may be assumed that, under the conditions investigated, dissociation of the TCNE—anthracene adduct takes place, accompanied by the abstraction of mobile hydrogen atoms located in the meso positions, with subsequent polymerization of anthryl radicals, leading to the formation of dia- and paramagnetic polymers (^{3}). Thus, the results obtained show that activation of anthracene by creating paramagnetic polymer particles in it can be accomplished not only by means of strong energetic action (^{5}). It is possible to create such systems (of the TCNE—anthracene adduct type) which, at comparatively low temperatures (below 200°), are capable of forming paramagnetic polymer products responsible for the manifestation of the effect of local activation in the inhibition of thermooxidative processes by these systems.

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