

ENHANCING THE EFFICIENCY OF ORGANIC PHOSPHITES AS INHIBITORS OF THE OXIDATION OF SOLID POLYPROPYLENE BY TRANSITION METAL IONS*

D. G. POBEDIMSKII, SH. A. NASYBULLIN, V. A. KURBATOV
and P. A. KIRPICHNIKOV

S. M. Kirov Chemico-technological Institute, Kazan

(Received 9 July 1976)

By reacting with peroxide radicals organic phosphites inhibit the oxidation of solid polypropylene (PP). A quantitative evaluation of the efficiency of two phosphites was carried out; the inhibiting efficiency of the phosphite containing masked phenoxy fragments in its molecule is higher by one order than that of the unsubstituted triphenylphosphite (as in the liquid phase). The efficiency of organic phosphites is greatly enhanced by additions of acetylacetonates of transition metals to a solid polymer. The observed critical effects are explained in terms of concepts of rapid kinetic chain termination by molecules of a phosphite coordinated in a complex with a metal chelate. It is demonstrated that the synergetic system phosphite + metal is most efficient when the ability of the metal to catalyze the oxidation of solid PP is lowest.

It is known [1-3] that organophosphorus compounds (phosphites) are inhibitors of the catalytic action of metal (Me) compounds in processes of oxidation and degradation of polymeric materials. However, the feasibility of using phosphites as anti-ageing agents for polymers (in the presence of Me leads to greatly accelerated ageing has been investigated only under conditions of autooxidation of molten PE [2, 3], which cannot provide a proper basis for a strict interpretation of the mechanism underlying the appearance of synergetic effects in the action of Me + phosphite systems, nor would it be possible under these conditions to assess quantitative characteristics of the inhibiting action of phosphites in the presence of Me and in their absence.

Accordingly an attempt was made to investigate regularities of the inhibiting action of aromatic phosphites during the initiated oxidation of solid PP, and the effect of enhancement of the efficiency of these phosphites in presence of acetylacetonates of Ni^{+2} , Co^{+2} , VO^{+2} , Fe^{+3} and Cr^{+3} was investigated.

The initiated oxidation of isotactic PP (85°, 650 torr O_2) was investigated on a manometric apparatus. Tests were carried out with powder form PP with particle sizes of less than 100 μ , viscosity average MW 490,000, melt index 1.9, degree of crystallinity[†] 80%.

* Vysokomol. soyed. A19: No. 2, 352-356, 1977.

† This parameter was determined by V. S. Minkin (by a pulsed NMR method).

The initial PP contained no hydroperoxide groups. Benzoyl peroxide (BP), concentration 5×10^{-2} mole/kg, was used as the initiator.

The rate w_0 of oxidation of the PP was not varied during an experiment and was constant under O_2 pressures exceeding 300 torr. The initiation rate w_i was not determined separately, but was calculated ($w_i = 3.8 \times 10^{-7}$ mole/kg·sec) from the Arrhenius equation of the rate constant for the radical decomposition of BP; cited in [4].

The oxidizability parameter of the polymer determined by us $k_2 [PH] / \sqrt{k_4} = 1.6 \times 10^{-4}$ mole^{1/2}kg^{-1/2} sec^{-1/2} was close to the value stated in [4].

Triphenylphosphite (TPP), tri(4-methyl-6-tert.butyl)phenylphosphite (TMBP) and the acetylacetonates of Ni^{+2} , Co^{+2} , VO^{+2} , Fe^{+3} , Cr^{+3} and the initiator were added to the PP in solution in methylene chloride or benzene.

The results showed that BP and TPP added to PP in equimolar ratio, do not interact at 85°, the initiator content in experiments involving acetylacetonates of metals remains constant in the course of the latter, and the depletion rate of the nitroxyl radical during the decomposition of BP in chlorobenzene, measured by EPR at 85°, is not increased by the introduction of catalytic additions of Me into the solution. This means that no catalytic decomposition of BP takes place in presence of the metal compounds.

Under conditions of solid phase oxidation of PP phosphites (P), as in reactions of oxidation of low molecular hydrocarbons [5], have only slight inhibiting properties: inhibited oxidation of the substrate appears only when considerable amounts of P are added, and a further increase in the concentration of P (TMBP) is accompanied by the appearance of short induction periods (τ) in oxidation, which are a linear function of the concentration of P. By measuring initial rates of oxidation w in the presence of P we determined from the slope of the anamorphosis

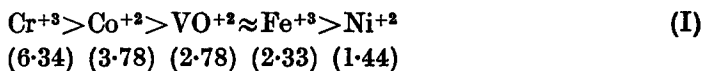
$$F = w_1/w(1 - w^2/w_0^2) = (fk_7/k_2[PH])[P]_0$$

(this relation was obtained on the assumption that reactions of pseudomolecular chain termination by a phosphite and bimolecular termination take place simultaneously) the relative constant for inhibition $fk_7/k_2 [PH]$ by a phosphite: for TMBP— 2.1×10^2 and for TPP, 2×10^1 kg/mole. The stoichiometric coefficient of inhibition f was determined from the slope of the experimental plot of $\tau = (f/w_i) [P]_0$ which, for TMBP, is 0.06 (there was no induction period for TPP).

The results obtained are significant in that they demonstrate properties common to phosphites as inhibitors whether for solid phase or liquid-phase reactions: 1) under solid phase conditions (as well as in low-molecular hydrocarbons) phosphite "autooxidation" chain transfer reactions take place rapidly; it is these reactions that are responsible for the low values of the stoichiometric coefficient of inhibition; 2) phosphites containing masked substituents (TMBP) are stronger inhibitors of chain termination than the unsubstituted TPP, and the ratio of parameters fk_7 for the foregoing phosphites remains approximately the same under solid phase conditions, as in liquid phase reactions.

The addition to PP of acetylacetonates of Ni^{+2} , Co^{+2} , VO^{+2} , Fe^{+3} and Cr^{+3} results in a catalyzed oxidation regime (Fig. 1) whereby, as the Me concentration rises, the oxidation rate increases (the exception being the vanadyl chelate; for

which catalysis of oxidation appears solely in the case of low concentrations of the chelate). Placing the chelates in the order of their ability to catalyze the oxidation of PP under the conditions adopted we have



As a measure of the catalytic activity we took the rate of oxidation in the presence of 10^{-3} mole/kg of metal-complex relative to the rate of the ordinary initiated oxidation. The observed mode of branching is apparently due, as in liquid

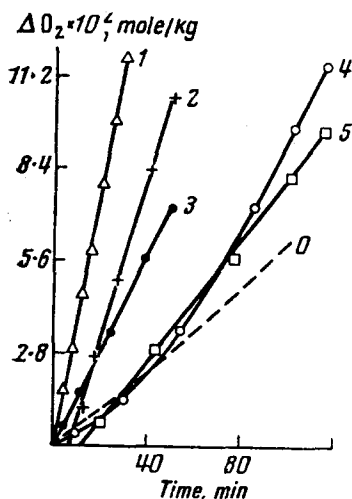


FIG. 1

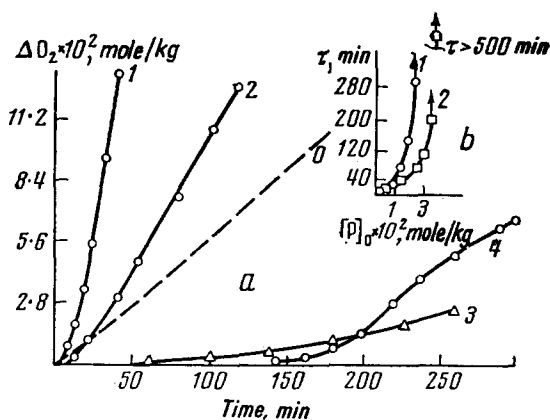


FIG. 2

FIG. 1. Kinetic curves of O_2 absorption by oxidizing PP in the presence of: $\text{Cr}(\text{acac})_3$ (1), $\text{Co}(\text{acac})_3$, (2) $\text{Fe}(\text{acac})_3$ (3), $\text{VO}(\text{acac})_3$ (4), $\text{Ni}(\text{acac})_3$ (5) and without additions (0), ($W_i = 3.8 \times 10^{-7}$ mole/kg·sec, 85°). Concentration of metal-complexes 10^{-3} mole/kg.

FIG. 2. Kinetic curves of O_2 absorption by oxidizing PP ($w_i = 3.8 \times 10^{-7}$ mole/kg·sec, 85°) in presence of 3×10^{-3} (1), 6×10^{-4} mole/kg $\text{Co}(\text{acac})_3$ (2), 2×10^{-2} mole/kg TMBP (3), system containing 6×10^{-4} mole/kg $\text{Co}(\text{acac})_3$ and 2×10^{-2} mole/kg TMBP (4) and similarly in the absence of inhibitors (0) (a) and induction period τ versus concentration: TMBP (1) and TPP (2) (b).

phase reactions of oxidation of hydrocarbons in the presence of organometal compounds, to Me catalyzed decomposition of PP hydroperoxide groups, formed in the oxidation process, to radicals. This is borne out by other factors, that is, first, at the end of an experiment the amount of PP hydroperoxide relative to the total amount of absorbed O_2 is 1.5–2 times lower, in presence of the catalyst, than in the absence of the latter (in the case of ordinary initiated oxidation the POOH content amounts to 40–50%); secondly, in the absence of O_2 and of the initiator the addition of chelates to PE containing OOH groups results in a lower POOH content.

Under these conditions phosphite addition leads to the appearance of well defined induction periods τ , after which the oxidation proceeds at a rate exceeding that for oxidation inhibited solely by a phosphite, which falls sharply when the concentration of P is increased (Fig. 2a). In the case of the chelates Ni^{+2} , Co^{+2} and Fe^{+3} , it was found that starting at a certain added phosphite concentration there is a non-controllable extension of the induction period—a critical phenomenon that was nevertheless absent in the case of the system involving the participation of $\text{Cr}(\text{acac})_3$.

It is of interest that contrary to model liquid phase reactions [5], a non-additive dependence of τ on the concentration of P appears for the triphenylphosphite as well (Fig. 2b, curve 2).

In the light of these results it appears that as in the oxidation of styrene and tetralin [5], the synergetic effects observed in PP are most probably due to the activation of reactivity (with respect to radicals PO_2) of the phosphite ligand in the complex with a metal-organic compound that emerges in the course of the reaction. It should be added that even under solid phase conditions the formation of an active (P...Me) complex takes place at high rates immediately after the mixing of the reagents. This is evident from the fact that when preheated (85° , 3 hr) in the absence of O_2 the initial system $\text{Ni}(\text{acac})_2 + \text{TMBP}$ in PP, given subsequent addition of the initiator, has the same (not stronger, as anticipated) inhibiting effect as in ordinary experiments.

Next, we anticipated that synergetic effects observed by us [5] during oxidation of the model system tetralin + TPP + $\text{VO}(\text{acac})_2$ would also occur in PP, where chain branching at the expense of radical decay of hydroperoxide groups of PP would be effectively suppressed, as in the model hydrocarbon, by the non-radical reaction of POOH with the phosphite catalyzed by vanadium ions.

Certainly, TPP additions to PP do lead to a marked reduction in the rate of $\text{VO}(\text{acac})_2$ catalyzed oxidation (a more marked reduction than in the presence of TPP by itself), although the latter effects is much less pronounced than under conditions of liquid phase oxidation of tetralin. Next, it was found that TMBP suppresses branching to a somewhat lesser extent than TPP, though the former, as a phosphite containing naked substituents, has a stronger inhibiting effect than the latter. At the same time the results of special tests showed that the rate of interaction with hydroperoxide groups of PE is lower for TMBP. It would appear from these facts that phosphites, along with chain termination in reactions with radicals PO_2 , also remove from the catalytic breakdown reaction OOH groups of PP, thereby suppressing the main source of chain branching.

Of major significance is the fact that at high chelate concentrations (3×10^{-3} mole/kg) phosphite additions have only a slight effect on the kinetics of O_2 absorption, although it was considered in [6], in view of special characteristics of the mechanism of the catalytic action of phosphites with hydroperoxides in solutions, that under these conditions the rate of catalytic breakdown of POOH by phosphites will be increased, and the inhibiting effect will consequently be stron-

ger. In fact, it was found that the model reaction of interaction of hydroperoxide groups of solid PE with TPP is not accelerated in the presence of catalytic amounts of $\text{VO}(\text{acac})_2$, while higher Me concentrations even lead to inhibition of the reaction (Fig. 3). When the metal is added, the polymer takes on a reddish violet colouring, which means that as in the liquid phase [7] a reaction of prior activa-

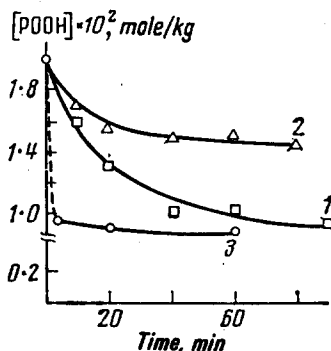
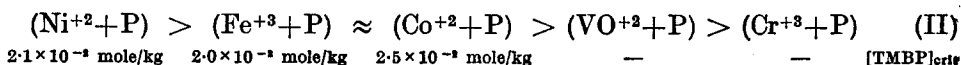


FIG. 3. Kinetic curves of the expenditure of hydroperoxide groups of PE ($M_w = 20,000$) during interaction with triphenylphosphite in the presence of 2×10^{-3} (1), 6×10^{-3} mole/kg $\text{VO}(\text{acac})_2$ (2) without a catalyst and in the presence of $\text{VO}(\text{acac})_2$ in concentrations below 10^{-3} mole/kg (3) $[\text{POOH}]_0 = [\text{TPP}]_0 = 2 \times 10^{-3}$ mole/kg.

tion of catalyst takes place. It follows from this that hydroperoxide groups form a complex with catalyst, although in all probability the latter reaction with P fails to take place (or is inhibited) because of diffusion hindrances. It appears that the catalyst, forming a complex with the hydroperoxide group, "screens" the latter from subsequent attack by the phosphite molecule. A similar pattern appears in the case of the BP initiated oxidation of low molecular molten PE: TPP additions bring only a slight reduction in the $\text{VO}(\text{acac})_2$ catalyzed oxidation.

Thus, the suppression of branching observed in processes of $\text{VO}(\text{acac})_2$ catalyzed oxidation of polyolefins becomes possible not only on account of chain termination by P molecules, but also in view of a non-catalytic reaction between the phosphite and OOH-groups of the polyolefin; the absence of catalysis of a reaction of POOH with P is due to special characteristics of the physical state of the polymers.

In the light of the experimental results we have the following order of efficiency of the synergetic systems



In addition, on comparing the latter order with order I regarding the catalytic activity of the metal-complexes, it can be seen that the synergetic effect of a system is inversely proportional to the ability of the metal-complex in the system to

catalyze oxidation. For instance, for phosphite+Cr(acac)₃ systems, the catalytic activity of Cr(acac)₃ being the highest among the metals examined, the critical phenomenon is altogether absent. On the other hand, the "critical" concentrations of TPP and TMBP for the studied systems containing acetylacetonates of Ni⁺², Co⁺² and Fe⁺³ are approximately equal.

In view of the regularities outlined above it seems that the antiradical activity of (P...Me) complexes, like that of stable radicals and phenol inhibitors [8] has been levelled out under solid phase conditions owing to the fact that the interaction of radicals and of the complex formed during the reaction is diffusion controlled, and the efficiency of one or other synergetic system depends mainly on the catalytic power of the metal-organic compound that the system contains. This comes to light convincingly in the case of the system Co(acac)₂+TMBP, for which the critical phenomenon disappears if the amount of the chelate being added is increased (five fold) to 3 × 10⁻³ mole/kg, while the rate of oxidation catalyzed by Co(acac)₂ is increased 3.7 fold.

Thus the formation of (P...Me) complexes that are active in chain termination steps through interaction with peroxide radicals is a common characteristic and is the factor giving rise to the appearance of synergetic effects when the oxidation of solid polymers is inhibited by mixtures of phosphites and metal-organic compounds; under solid phase conditions the factor determining the efficiency of a P+Me system is the extent to which the metal complex in the latter is capable of catalyzing oxidation. It is of considerable significance that given the quantitative regularities of the action of the P+Me systems examined here, one is able to offer an unambiguous explanation of the known facts [2, 3] relating to stabilization of the properties of polymeric materials containing residues of polymerization catalysts by means of additions of organophosphorus inhibitors.

Translated by R. J. A. HENDRY

REFERENCES

1. P. A. KIRPICHNIKOV and N. A. MUKMENEVA, Sbornik. Stareniye i stabilizatsiya polimerov (Ageing and Stabilization of Polymers). Izd. "Khimiya", 168, 1966
2. N. A. MUKMENEVA, L. Kh. SABIROVA, V. Kh. KADYROVA and P. A. KIRPICHNIKOV, Plast. massy, No. 1, 51, 1975
3. N. A. MUKMENEVA, A. G. AKHMADULLINA, L. Kh. SABIROVA, E. G. CHEBOTAREVA and P. A. KIRPICHNIKOV, Vysokomol. soyed. B18: 108, 1976 (Not translated in Polymer Sci. U.S.S.R.)
4. Yu. B. SHILOV and Ye. T. DENISOV, Vysokomol. soyed. A14: 2385, 1972 (Translated in Polymer Sci. U.S.S.R. 14: 11, 2780, 1972)
5. D. G. POBEDIMSKII, Sh. A. NASYBULLIN, V. Kh. KADYROVA and P. A. KIRPICHNIKOV, Dokl. AN SSSR, 226: 634, 1976
6. D. G. POBEDIMSKII, Sh. A. NASYBULLIN, E. G. CHEBOTAREVA, P. A. KIRPICHNIKOV and L. L. BUCHACHENKO, Dokl. AN SSSR 220: 641, 1975
7. E. GOULD, R. HIATT and K. IRWIN, J. Amer. Chem. Soc. 90: 4573, 1968
8. N. EMANUEL and G. ZAIKOV, Vysokomol. soyed. A17: 2122, 1975 (Translated in Polymer Sci. U.S.S.R. 17: 9, 2449, 1975)