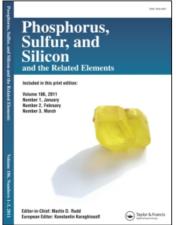
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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

NEW ASPECTS IN THE MECHANISM OF INHIBITORY ACTION OF SULPHUR CONTAINING METAL COMPLEX COMPOUNDS IN THE OXIDATION OF HYDROCARBONS

Slavi K. Ivanov^a

^a Institute of Organic Chemistry of Bulgarian Academy of Sciences, Sofia, Bulgaria

To cite this Article Ivanov, Slavi K.(1979) 'NEW ASPECTS IN THE MECHANISM OF INHIBITORY ACTION OF SULPHUR CONTAINING METAL COMPLEX COMPOUNDS IN THE OXIDATION OF HYDROCARBONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 141 - 142

To link to this Article: DOI: 10.1080/03086647908080344 URL: http://dx.doi.org/10.1080/03086647908080344

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NEW ASPECTS IN THE MECHANISM OF INHIBITORY ACTION OF SULPHUR CONTAINING METAL COMPLEX COMPOUNDS IN THE OXIDATION OF HYDROCARBONS

Slavi K. Ivanov

Institute of Organic Chemistry of Bulgarian Academy of Sciences, Sofia, Bulgaria

The first studies dealing with the antioxidizing action sulphur containing organic compounds in the stabilization of petroleum products, polymers, rubber etc., suppose an interaction of these inhibitors with hydroperoxides and the decomposition of the latter to molecular inactive products. The absence reaction of the peroxide radicals, leading the chain of the autoxidation. with the inhibitor is presumed. The initiating properties of the inhibitors-peroxide decomposers were known/1,2.3/.As a result of our and other authors' investigations was shown, that the sulphur containing antioxidants re act with the peroxide radicals and they are able to initiate the autoxidation processes, because in the oxidation of hydrocarbons in the simultaneous presence of hydroperoxides sulphur containing compound, a prooxidizing effect is observed i.e. acceleration of the oxidation in a certain period of the process/4.5.6/.It was observed, that a period of rapid oxida tion.followed by autoretardation of the oxygen absorption, appears in the oxidation of tetraline and cumene, respectively in the presence of tetraline and cumene hydroperoxides metal dialkyldithiophosphates, dithiocarbamates and dithiolates. The oxidation of cumene and tetraline, initiated by AIBN at 600 in the presence of zinc dithiophosphate, zinc dithiocarbamate and nickel dithiolate, proceeds with the appearance of induction periods. In this way, the existence of interaction between RO and sulphur containing metal complex compounds is verified

The stoichiometric coefficient of inhibition depends on the concentraton of the used inhibitor, which is a proof that in the induction period, the inhibitar is consumed not only by an interaction with the peroxide radicals, but by means of another reaction. This fact explains the existence of different values of the stoichiometric coefficients, measured by different groups of authors using different initial concentrations of the studied inhibitors. At a definite correlation between AIBN and sulfur containing complexes in the oxidation of cumene, an effect of oscillation is observed i.e. the induction period is followed by a periodical change of the oxygen absorption rate /7.8/.The frequence of oscillation increases with time and the differences between the inflexion become greater. A similar effect was observed in the initiated by AIBN oxidation of cumene in presence of Zn-bis(diisopropyl)dithiophosphate-(I), Zn-bis(diethyl)dithiocarbamate-(II), Ni-bis(diphenylethylene)dithiolate-(III). The existence of oscillating effect obviously is due to the competition of two parallel processes-the absorption and the liberation of gas. With the help of mass spectral analysis, it was shown that as a result of the reaction of (I), (II], (III) inhibitors and hydroperoxides, oxygen is liberated. The use of acceptors of synglet oxygen(9,10-diphenylantracene) shows that the liberated gas is synglet oxygen/9/.

REFERENCES

- 1.Denison G.H., Condit P.C., Ind. Eng. Chem., 36,477 (1944); ibid, 37 1102 (1945); ibid, 41,944 (1949)
- 2.Kennerly G.W., Patterson W.I., Ind. Eng. Chem., 48, 1917 (1956) 3. Iarson R., Scientific Iubrification, August, 12 (1958)
- 4. Ivanov S.K., Shopov D., Compt. rend. Acad. bulg. Sci., 18,845 (1965)
- 4.Ivanov S.K., Snopov D., Compt. rend. Acad. bulg. Sci., 25, 645, (1972)
- 6.Ivanov S.K., Compt.rend.Acad.bulg.Sci., 20, 1153 (1967) 7.Ivanov S.K., Kateva J.D., J.Pol.Sci., part C, in press. 8.Kateva J.D., Ivanov S.K., J.Pol.Sci., part A, in press.

- 9. Ivanov S.K., KatevaJ.D., Compt.rend. Acad. bulg. Sci., in press.