THEORETICAL ANALYSIS OF THERMAL DESTRUCTION OF DIMETHYL PHOSPHATES IMMOBILIZED ON DISPERSED SILICA SURFACE

V.V. Kukueva[1], O.A. Kirilov[1], A.G. Grebenyuk[2], and V.V. Lobanov[2]

[1]Institute of Fire Security, Onoprienko Str. 8, 18034 Cherkasy, UKRAINE
[2]Institute of Surface Chemistry, National Academy of Sciences
Gen. Naumov Str. 17, 03680 Kyiv-164, UKRAINE

Abstract

The calculations on the electronic and space structure have been carried out for both trimethyl phosphate molecule and that supported at silica surface within the frameworks of the SCF MO LCAO MNDO valence approximation. The routes of these systems destruction have been studied. The decomposition of trimethyl phosphate molecule chemically immobilized onto fumed silica surface has been shown to occur with absorption of small heat quantity (~19.1 kcal/mol). This explains a high effectiveness of the use of silicas modified by organic phosphorus derivatives as active components of fire-extinguishing powders.

Introduction

Any burning is first of all a chemical reaction of the combustible mixture components accompanied by heat emitting and creating of disperse kind mass-transfer processes in gas. That is why all the phenomena of burning and fire-extinguishing are closely connected with ideas and rules of chemical kinetics and first of all with the concept of the rate of chemical reaction running under non-isothermal conditions. Then the heat evaluated due to reaction accelerates the latter, in according to the Arrenius rule. The availability of such a correlation is a high degree characteristic of the most of burning phenomena. Owing to this correlation between mixture heating due to reaction and acceleration of the latter a heat self-accelerated avalanche arises that is often perceived as a self-ignition. However it has been shown in [1] that self-ignition has not consistently a heat nature but there is another type of self-ignition based on a chain chemical oxidation reaction. A chain branched process gives rise to active particles – radicals in the substances, their quantity being quickly rising in the time as a sequence of chain branching. Thereafter as the flame spreads they play a role of active sites stimulating chemical process what is a characteristic of the chain mechanism of chemical reaction. A suitable partner can be selected for almost each active radical, interaction between them resulting in the formation of less reactive particle (the latter is most often a molecule in the singlet state) followed by the chain rupture. In particular, just this can take place on addition of some inorganic or organic substances showing inhibiting properties into the hydrogen flame that can be performed conditionally as a totality of active sites ($O^\bullet$, $H^\bullet$, $OH^\bullet$, $HO_2^\bullet$). An active site can create two new second chains with definite probability when enters the reaction of main chain continuation. When branched, these second chains form tertiary chains ad so on. Thus, the quantity of chains should arise in the time. Simultaneously all these chains should be interrupted, for example, when an active particle meets the inhibitor thermal decomposition products [1].

Background

The mechanism of the hydrogen flame suppression with disperse compositions can be caused either by a heat interaction of solid and gaseous phases (the physical factor – a decrease in the temperature of burning mixture) or by chemical inhibiting, or by their combination (as a result of the chain rupture the heat evaluation ends and the temperature is reduced and becomes below the ignition level). There is a reason to believe that the high action effectiveness of the fire-extinguishing powders is conditioned mainly by chemical factors rather by than physical ones [2]. In other words, the powder supply into the ignition zone should result in increasing the reaction active site ruin rate. Moreover, a recombination reaction of "hot" molecules and radicals can take place on solid powder particle. The solid particle plays a role of an effective reservoir for their excitation energy dissipation. It should be expected that the less ordered is the particle structure, the more wide is the spectrum of the energy (rotational, vibration, electric) absorption of "hot" atoms and molecules. In principle, the powder action can be caused by both heterogeneous ruin rate of reactive chain carriers and homogeneous reactions following the transition of the powder particle decomposition products into the gas phase. There are considerable differences in the conformities to natural laws of the flame suppression that are conditioned by differences in the chain carrier types reacting with the inhibitor. The effect of extinguishing consists in the deactivation of the flame active sites (FAS) $Y^\bullet$ ($O^\bullet$, $H^\bullet$, $CH_3^\bullet$, $OH^\bullet$, $HO_2^\bullet$, and so on) at the surface of fire-extinguishing powder particle that is in the flame torch or in the gas phase including the thermal decomposition products of inhibiting agent [3].

Basing on comparing the rate of chain branching process with that of the hydrogen atom ruin in the reactions with decomposition products of fire-extinguishing powders, an assumption was made [4] on the availability of combined homogeneous-heterogeneous inhibiting mechanism. Moreover, it should be taken into consideration that the dissociation energy of adsorbed molecule may be lesser than that of dissociation of the same molecule in gas phase. If the dissociation activation energy is considered to be close to that of dissociation itself or to coincide with it, the rate of molecule dissociation on surfaces should be greater that that in gas phase what is conditioned by chemical sorption processes. In this case the surface should play a role of a catalyst of radical recombination reactions. It is important for the further elucidation of the character of interaction of the flame active sites with substances-inhibitors to compare the energy of the probable dissociation paths of both isolated and immobilized molecules.

There are widely used phosphorus organic compounds among various chemical additives to fire-extinguishing powders. Thus, trimethyl phosphate (TMP) has been shown [5] to be an effective burning inhibitor. Firstly the reaction mechanism of phosphorus oxides with radicals – flame active sites was studied by Twarowski [6] who examined a catalytic effect of phosphorus oxides on the $H^\bullet$ and $OH^\bullet$ recombination reaction. It was shown in the same work by an experiment that on addition of TMP into flame the $HPO_2^\bullet$, $PO_2^\bullet$ and $PO^\bullet$ particles (formed due to thermal decomposition of trimethyl phosphate) are the most active inhibiting ones. But no qualitative data (deactivation energy, rate of recombination reaction) were obtained concerning the interaction of these particles with the flame active sites. Obviously it is connected, to our mind, with the complexity of experimental measurements at elevated temperatures.

Earlier it was shown in the experimental studies on the investigation of thermal stability of phosphorus-containing fumed silica [7] that a presence of chemically sorbed phosphorus compounds at silica surface bound with silicon atoms via oxygen bridge leads to the considerable diminishing of the C-H bond strength in the $\equiv$Si-O-PH(=O)-CH_3 groups. This fact

testifies an opportunity of to use trimethyl phosphate immobilized onto silica surface in order to diminish the heat of decomposition of the fire-extinguishing powder.

Models and Method

In the case when direct experimental investigations are difficult or impossible due to one or other cause theoretical approaches (in particular, methods of modern quantum chemistry) become an invaluable tool for obtaining qualitative data. The rupture energies are calculated in the given work of both free TMP molecule and that grafted to fumed silica surface simulated by a $HO-Si[OSi(OH)_3]_3$ cluster within the frameworks of the SCF MO LCAO MNDO valence approximation [8] according to the technique described in [9].

Results and Discussion

The heat effects (ΔH°_{298}) of the isolation reactions of methyl and oxymethyl particles bearing electric charge of –1, 0, and +1 from free TMP molecule in the ground state are performed in the Table 1. These effects were computed as differences between the heat of formation of the parent molecule and the sum of analogous values of the destruction products, the charge and spin state of the system destroyed being kept.

Table 1. Enthalpies (ΔH°_{298}) of the destruction reactions of free trimethyl phosphate molecule (kcal/mol).

N	Destruction Products	Reaction Enthalpies
1	$OPO(OCH_3)_2{}^\bullet + CH_3{}^\bullet$	319.0
2	$OPO(OCH_3)_2{}^+ + CH_3{}^-$	328.8
3	$OPO(OCH_3)_2{}^- + CH_3{}^+$	220.3
4	$OP(OCH_3)_2{}^\bullet + OCH_3{}^\bullet$	143.5
5	$OP(OCH_3)_2{}^+ + OCH_3{}^-$	343.6
6	$OP(OCH_3)_2{}^- + OCH_3{}^+$	194.9

It is seen from the table considered that in isolated TMP molecule the rupture of P-O bond followed by the formation of two radicals

$$OP(OCH_3)_3 \rightarrow OPO(OCH_3)_2{}^\bullet + CH_3{}^\bullet$$

is somewhat greater ($\Delta H^\circ_{298} = 319$ kcal/mol). Hence, the probability of the methyl radical formation (that is one of active sites of hydrocarbon flame) is very low when the inhibitor molecule disintegrates. This is another weighty argument in favor of the opportunity of TMP use as an inhibiting component of fire-extinguishing compositions.

Accordingly to the data we obtained the ionizing potential of the $OCH_3{}^\bullet$ particles is relatively small (7.3 eV) (experimental value is of 8.2 [10]) what testifies the easiness of the unpaired electron isolation from the $OCH_3{}^\bullet$ radical, this electron is capable in its turn to interact with surface active sites and so to deactivate them. Thus, the data obtained for the TMP destruction in gas phase testify the easiness of radical particles formation that can make an inhibiting impact along with free electrons generated due to ionizing of radicals.

Analogous calculations on the TMP molecule destruction energy were carried out for the system simulated for its chemically sorbed state at the fumed silica surface (see Fig.). The $\equiv$Si-O-PO(CH$_3$)$_2$ bond appeared to be the most weak one, the corresponding value of the rupture energy being only of 19.1 kcal/mol (see Table 2).

Table 2. Enthalpies (ΔH°_{298}) of the destruction reactions of dimethyl phosphate groups immobilized on silica surface (kcal/mol).

N	Destruction Products	Reaction Enthalpies
1	[(HO)$_3$SiO]$_3$SiO$^\bullet$ + OP(OCH$_3$)$_2$$^\bullet$	19.1
2	[(HO)$_3$SiO]$_3$SiO$^-$ + OP(OCH$_3$)$_2$$^+$	193.6
3	[(HO)$_3$SiO]$_3$SiO$^+$ + OP(OCH$_3$)$_2$$^-$	226.2

$\bigcirc$ **O** $\quad$ ⬤ **Si** $\quad$ ● **C** $\quad$ • **H**

Fig. A schematic presentation of the cluster (CH$_3$O)$_2$PO-OSi[OSi(OH)$_3$]$_3$

As a result of thermal destruction of the phosphorus-containing fumed silica in gas phase the OP(CH$_3$)$_2$$^\bullet$ radical appears that make an inhibiting influence on the flame active sites, and an inhibiting site is generated at the solid surface with a high degree of spin density localizing (at the surface oxygen atom (0.82)). This site is capable to capture and deactivate practically all the known types of flame active sites because the energy they yield dissipates
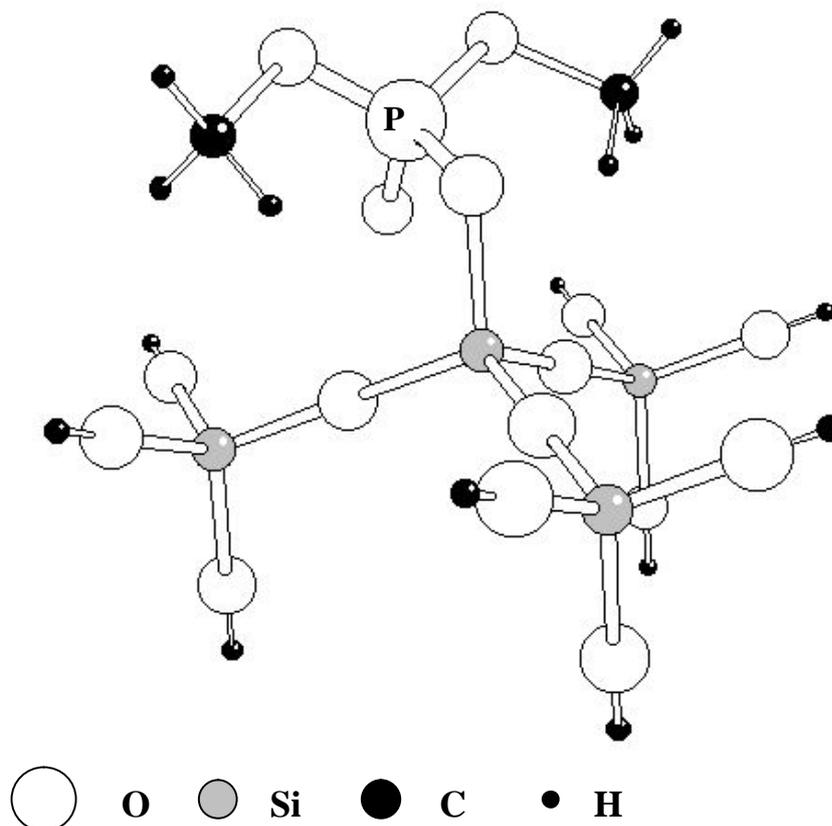
effectively along the bonds of solid support. This fact argues for the perspective of silica use as a support for the prolongation of inhibitor action.

Conclusions

Thus, a theoretical investigation by quantum chemical calculations not only gives an opportunity to foresee real ways of decomposition of the active substance of fire-extinguishing powders, but also proves a greater activity of the inhibitor grafted onto silica surface than that of isolated state what can be used for the prolongation of inhibitor action via immobilization onto fumed silica. Such kind calculations give a real opportunity to examine complicated physicochemical processes at molecular level for selection of the most effective conditions of the flame inhibition.

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