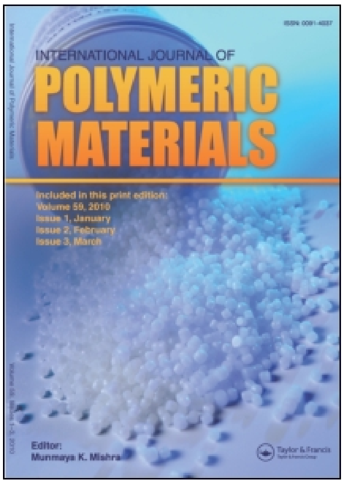

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Structural-Chemical Conception of Stabilization of Aromatic Polymers as Exemplified by Arylene Carboranes

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The paper discusses the specific features of thermal behaviour of carborane-containing polymers and the stabilizing effect of the carborane groups as exemplified by arylene carboranes. The results obtained explain as a whole the stabilizing effect of aromatic polymers by carborane-containing additives.

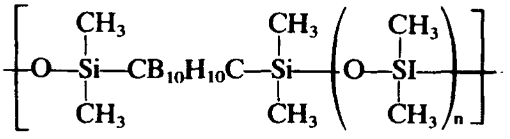
KEYWORDS: Polyarylene carborenes, structural-chemical conception, degradation, stabilization, carborane groups, thermostable fragments

At the present time the requirements for a prolonged thermal stability of polymers, the working temperatures of the corresponding composites, considerably exceed those of the stability of chemical groups and chemical bonds which form even the most thermally stable polymers (cyclo-chain polyheteroarylenes, polyorganosiloxanes). The stabilizers of thermal and thermal-oxidative degradation acting by the known classical mechanisms cannot be effective at 350–400°C, at least for a prolonged time. At the same time it has sufficiently long been established in practice that the polymers with carborane-12 groups in the macromolecule make it possible to achieve higher working temperatures of polymeric materials.[1]

A sufficient number of papers dealing with investigations and explanations of the specific features of thermal behaviour of carborane-containing polymers and the stabilizing effect of the carborane groups was published. But most often the conceptions developed in them are either of purely phenomenological or of insufficiently well-founded, hypothetical character due to complex investigations of chemical transformations especially in three-dimensional polymeric matrix. The present lecture reports the results of investigations on the mechanisms of carborane-12 transformations by the action of high temperatures and oxygen that can explain this unusual thermal behaviour of carborane-containing polymers and formulate a general approach to stabilization of polymeric materials intended for operation at elevated temperatures.

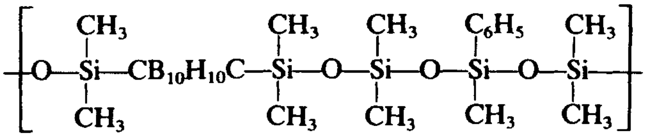
In the last two decades almost all known classes of polymers containing carborane-12 groups in the backbone or as side groups have been prepared. Investigations of their properties showed that the introduction of carborane groups into the polymer chain increases polymer thermal stability and their composites, this showing itself most effectively in case of aromatic polymers. A similar result can be achieved by introduction of carborane-containing additives into polymers primarily such as aromatic derivatives. Thus it can be said about the effect of carborane-12 groups stabilizing thermal and thermal-oxidative degradation of aromatic polymers.

In the behaviour of carborane-containing polymers under the action of elevated temperatures and oxygen a number of specific features can be marked which differentiate them from that of their ordinary analogs. For instance, under conditions of thermal-oxidative degradation the chemical transformations in the matrix of carborane-containing polymers are observed in most cases at lower temperatures (200–350°C) that allows for classifying them as thermostable polymers in the adopted meaning of this word.[2] Unusual small weight losses at high temperatures is the second most essential specific feature of carborane-containing polymers. In this case, for instance, the coke residue of polyarylates on heating in an inert atmosphere is slightly higher than on heating in air. This shows that the high coke residue is not sure to be caused only by oxidation with the formation of a large mineral residue. The coke residue of polyheteroarylene-carboranes is 83–88% at 900°C.[3] The polymers not containing carborane groups decompose in air practically completely at 600–650°C.



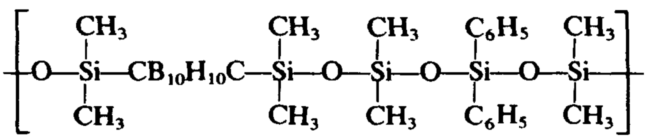
$$\left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-CB_{10}H_{10}C-\overset{CH_3}{\underset{CH_3}{Si}}\left(-O-\overset{CH_3}{\underset{CH_3}{SI}}-\right)_n\right]$$

I



$$\left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-CB_{10}H_{10}C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{C_6H_5}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]$$

II



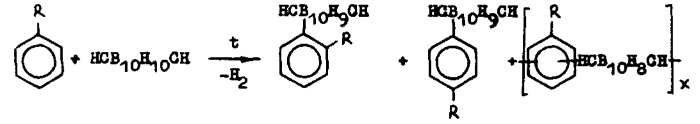
$$\left[-O-\overset{CH_3}{\underset{CH_3}{Si}}-CB_{10}H_{10}C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{C_6H_5}{\underset{C_6H_5}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]$$

III

It should be noted that essential increase in the coke residue takes place only if the polymer chain contains both carborane and aromatic fragment. Thus if dimethylcarboranesilicone polymer with structure I and $n = 3$ loses at 900°C 50% of weight, and the polymer with the same n and with one phenyl group (II) loses only 16.5% and the polymer with two phenyl groups (III) 13%. This means that the replacement of one or two methyl groups by phenyl ones in a not long siloxane fragment makes crosslinking processes more active thus increasing the yield of secondary structures. These processes are confirmed by the presence of two maximum on the curve of hydrogen evolution against temperature for polymers II and III. The first maximum is observed at 490–510°C, and the initial temperature of hydrogen evolution is 375–380°C. The second maximum at 620–630°C coincides with that of hydrogen evolution in dimethylcarboranesiloxane polymers of structure I. The total amount of evolved hydrogen increases considerably.[4] An interesting specific feature can be observed when investigating the influence of carborane group content on thermal decomposition of copolyarylates, for instance 9,9-bis(4-hydroxyphenyl)-fluorene, tetephthalic acid and 1,2-bis(*p*-carboxyphenyl-*o*-carborane.[5] The plot of decomposition rate and the coke residue against the residues of 1,2-bis(*p*-carboxyphenyl)-*o*-carborane on heating up to 900°C have two sections different in nature. With its content above 25 mol-% in copolymer a slight linear dependence between decomposition rate and the coke residue yield on copolymer composition is observed. If its content in copolymer is less than 25 mol-%, the decomposition rate drastically increases and the coke residue amount decreases. The temperature range of intense decomposition of copolymers with a 25–100% content of 1,2-bis(*p*-carboxyphenyl)-*o*-carborane is the same and equals 420–590°C. A similar linear dependence can be observed when studying thermal decomposition of mixed resite consisting of phenolocarboraneformaldehyde oligomer (PCF) based on 1,2-bis(4-hydrooxyphenyl)-*o*-carborane and classical phenolformaldehyde resol-300.[6] Compounds such as aromatic hydrocarbon and phenols characteristic of homolytic decomposition of ordinary resites are practically absent. Thus the available information demonstrates the absence of linear dependence between the carborane group content in polymer and the decrease in decomposition rate and weight loss that they cause. The fact that the introduction of carborane groups considerably decreases the content of aromatic compounds in the product of thermal decomposition of polymers agrees well with the observed total low weight losses.

It is established at present that this stabilizing effect of carborane groups is based on the ability of carbotane-containing polymers to form network systems during thermal and thermal-oxidative decomposition as a result of reactions with carborane group participation.[7] Investigations on model compounds gave conclusive proofs of the occurrence of these processes and their radical character,[8] although the chemical aspect of these processes remained unknown. We have found that these processes are the reactions of homolytical arylation of carboranes-12 which include the reactions of high-temperature arylations of *m*-carboranes directly with aromatic compounds, the arylation caused by radical sources (so-called the reaction of aromatic homolytical substitution), and the oxidative arylation under the action of oxygen and moderate temperatures.

The reaction of high-temperature homolytical arylation of carboranes-12 is believed to be mostly responsible for high thermal characteristics of carborane-containing polymers, in particular because it takes place at temperatures of intense decomposition of most of thermally stable, as a rule, aromatic polymers being a competitive reaction of synthesizing new secondary structures. Arylation occurs at above 400°C as follows:



The reaction gives largely polymeric products that is connected with polyfunctional character of both *m*-carboranyl and aromatic groups. And at conversion degrees above 95% infusible and insoluble three-dimensional polymers with an equimolar content of carborane and aromatic groups are forming. The resulting products, in particular B-aryl-*m*-carboranes reveal a complex isomeric composition which is connected with the presence of four non-equivalent positions in the *m*-carborane cage and two in the aromatic cycle (the *m*-position does not take part in this reaction).

The nature of aromatic cycle substituent influences the composition of the resulting B-aryl-*m*-carboranes. This is explained by that the *m*-carboranyl groups may demonstrate either positive inductive effect (in position 9) or negative one (in position 2).[9] Table I shows the composition of B-aryl-*m*-carboranes prepared by thermal condensation. it can be seen from the Table that the inductive effect of substituent in this reaction leads to some predominant formation of an isomer by position in the *m*-carboranyl group in which the significance of inductive effect is contrary to that of substituent. There is a correlation with the Hammets-constants both in case of *p*- and *o*-substitution in the aromatic cycle for the logarithm of the ratio of formation rates of 2- and 9-aryl-*m*-carborane isomers (proportional to the difference of formation activation energies) (Figures 1, 2).

The nature of aromatic compound considerably effects the rate of high-temperature arylation. Thus in the series of aromatic polycyclic hydrocarbons the reaction rate increases, as a rule, with increasing number of cycles, as seen in Table II showing the apparent constants for several aromatic compounds. The relative reaction rates (reaction rates with benzene are taken to be the unity) correlates in this case with the calculated values of localization energies[10] for

TABLE I

Composition of B-aryl-*m*-carboranes prepared at $T = 440°C$

	Content of *p*-isomers, %			Content of *o*-isomers,			Ratio of 2- and 9-isomers		
Substituent	2-	4- and 5-	9-	2-	4- and 5-	9-	*p*-	*o*-	Ratio of *o*-isomers
H—	21.5	53.5	15.0	—	—	—	1.43	—	—
CH_3—	20.1	62.8	17.1	24.9	59.0	16.1	1.18	1.55	1.62
C_6H_5—	19.6	62.4	18.0	20.7	60.3	19.0	1.08	1.09	1.73
$(CH_3)_3Si$—	20.1	62.5	17.4	22.0	63.0	15.0	1.15	1.47	2.02
CH_3O—	22.3	61.9	15.8	24.4	63.5	12.1	1.41	2.02	1.41
C_6H_5O—	16.9	67.6	15.5	19.2	65.2	15.6	1.09	1.23	1.65
Cl—	17.8	62.0	20.2	24.6	47.2	28.2	0.88	0.83	2.34
CF_3—	15.3	61.4	23.3	20.2	58.0	21.8	0.65	0.92	1.46

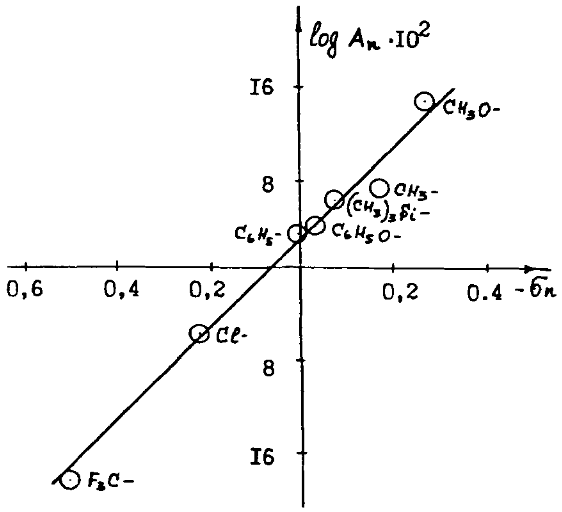


FIGURE 1 Dependence of the logarithm of concentration ratio of *p*-isomers of 2- and 9-aryl-*m*-carboranes (log An) on the Hammet constants 6n.

radical substitution in the aromatic series. This function is given in Figure 3. The effect of *m*-carborane concentration on the arylation product composition is a peculiar feature of the reaction. We believe that it is directly connected with the above-mentioned absence of proportional dependence between the content of carborane groups in the polymeric systems and the effect of decrease in decomposition rate and weight loss. Figure 4 shows the ratio of 2- and 9-phenyl-*m*-carborane isomers as a function of the ratio of initial *m*-carborane and benzene concentration at 440°C and low (~5%) conversion degrees. As can

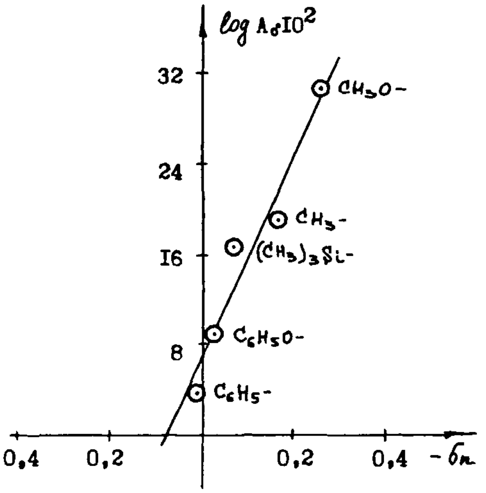


FIGURE 2 Dependence of the logarithm of concentration ratio of *o*-isomers of 2- and 9-aryl-*m*-carboranes (log Ao) on the Hammet constants 6n.

TABLE II

Rate constants of *m*-carborane arylation at $T = 460°C$

Compound	K 10^4 dm^3/mol sec	$K/K_{C_6H_6}$
Benzene	1.44	1.00
Diphenyl	1.83	1.27
Naphthalene	1.71	1.19
Phenanthrene	3.13	2.17
Pyrene	4.73	3.28
Anthracene	13.13	9.12
Chlorobenzene	7.60	5.28

be seen, with increasing *m*-carborane concentration the fraction of isomer 2-increases, and the ratio of isomers 2- and 9- approaches to a certain constant value. With decreasing *m*-carborane concentration the fraction of isomer 9-increases, and the isomer ratio also approaches to a certain constant value. The bend point on this curve corresponds to 20 mol-% of *m*-carborane. We believe that these data indicate that with low *m*-carborane concentrations the mechanism of high-temperature arylation differs from that with moderate and high concentrations. With decreasing *m*-carborane concentration the reaction selectivity is also impaired, and the yield of side products, in this case diphenyl, increases, as seen in Figure 5 which demonstrates the mole ratio of diphenyl and B-phenyl-*m*-carboranes yield as a function of the ratio of initial benzene and *m*-carborane concentrations.

Investigation of the kinetics of *m*-carborane arylation with naphthalene leading to the formation of B-(β-naphthyl)-*m*-carboranes with random isomer ratio at conversion degrees up to 30% and 440–490°C made it possible to find the

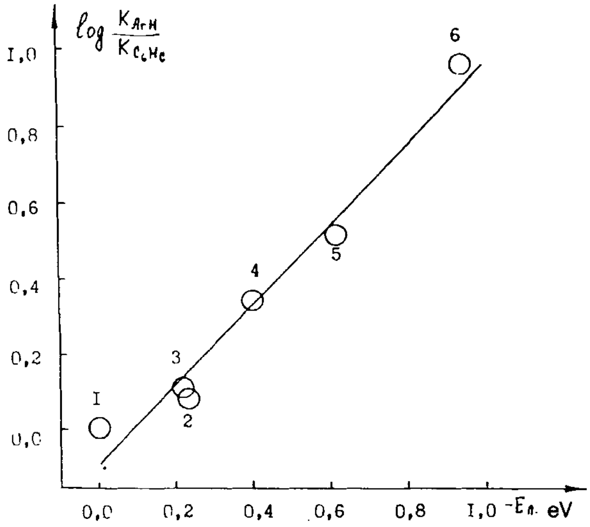


FIGURE 3 Dependence of the logarithm of relative reaction rates of relative localization energies. 1—benzene, 2—naphthalene, 3—diphenyl, 4—phenanthrene, 5—pyrene, 6—anthracene.

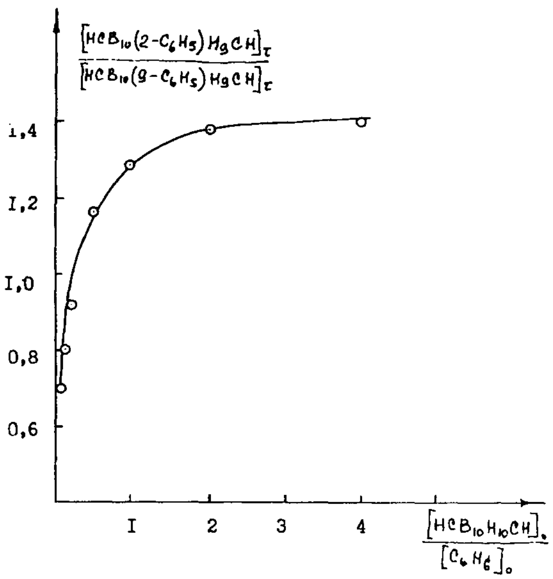


FIGURE 4 Dependence of the ratio of 2- and 9-phenyl-*m*-carborane isomers on the ratio of initial concentrations of *m*-carborane and benzene at 440°C $[C_6H_6]_0[HCB_{10}H_{10}CH]_0$ = constant.

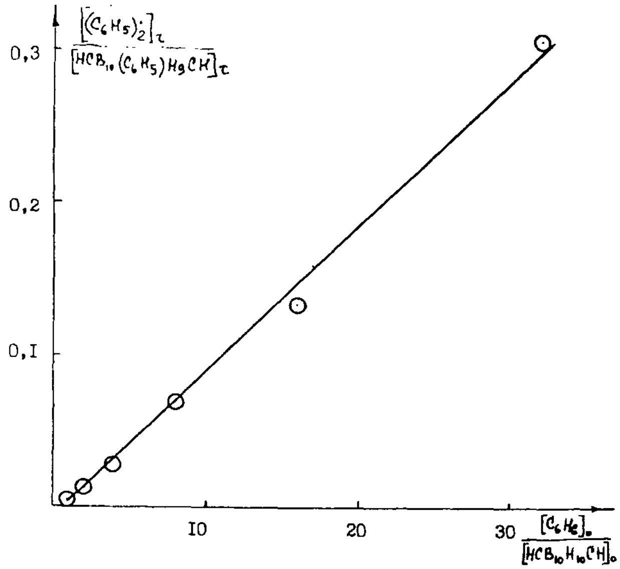


FIGURE 5 Dependence of the ratio of diphenyl and B-phenyl-*m*-carborane concentrations on the ratio of initial concentrations of benzene and *m*-carborane at 440°C. $[C_6H_6]_0[HCB_{10}H_{10}CH]_0$ = constant.

dependence of reagent consumption rate on their concentrations described as follows:

$$-\frac{d[\mathrm{HCB_{10}H_{10}CH}]}{d\tau} = -\frac{d[\mathrm{C_{10}H_8}]}{d\tau} = K[\mathrm{HCB_{10}H_{10}CH}]_0^{0.95\pm0.04}[\mathrm{C_{10}H_8}]_0^{1.01\pm0.03}$$

where

$$K = (6.3 \cdot 10^{11.0\pm1.0})\exp\left(-\frac{221\pm6}{RT}\right)\ \mathrm{dm^3/mol\ sec}$$

The available facts allow for presenting the high-temperature arylation as a chain radical process of addition of *m*-carborane to aromatic compounds

$$\mathrm{ArH} \xrightarrow{k_0} \mathrm{Ar}^{\cdot} \qquad (1)$$

$$\mathrm{Ar}^{\cdot} + \mathrm{BH} \xrightarrow{k_1} \mathrm{B}^{\cdot} + \mathrm{ArH} \qquad (2)$$

$$\mathrm{B}^{\cdot} + \mathrm{ArH} \xrightarrow[k_3]{k_2} \mathrm{ArHB}^{\cdot} \qquad (3)$$

$$\mathrm{ArHB}^{\cdot} + \mathrm{BH} \xrightarrow{k_4} \mathrm{ArH_2B} + \mathrm{B}^{\cdot} \qquad (4)$$

$$\mathrm{ArH_2B} \xrightarrow{k_5} \mathrm{ArB} + \mathrm{H_2} \qquad (5)$$

$$\mathrm{ArHB}^{\cdot} + \mathrm{B}^{\cdot} \xrightarrow{k_6} \mathrm{ArB} + \mathrm{BH} \qquad (6)$$

where BH—*m*-carborane, ArH—aromatic compound. If $k_3 \gg k_4[\mathrm{BH}]$, the reagent consumption rate will be determined by the expression

$$-\frac{d[\mathrm{BH}]}{d\tau} = -\frac{d[\mathrm{ArH}]}{d\tau} = k_4\left(\frac{k_2}{k_3}\right)^{1/2}\left(\frac{k_0}{k_6}\right)^{1/2}[\mathrm{ArH}][\mathrm{BH}] \qquad (7)$$

and the length L of the kinetic chain by the expression

$$L = k_4\left(\frac{k_2}{k_3}\right)^{1/2}\left(\frac{1}{k_0k_6}\right)^{1/2}[\mathrm{BH}] \qquad (8)$$

The length of the kinetic chain of reaction calculated from the literature data on the rate constants of pyrolysis (k_0) of a number of aromatic compounds[11] and from the experimental values of arylation rate constants for *m*-carborane concentration 0.399 mol/dm^3 is 38 for benzene, 1400 for napthalene and 36 for phenanthrene. For *m*-carborane/benzene ratio equal to 1:4 (experiment in Figure 4) the *m*-carborane concentration is 0.082 mol/dm^3 that corresponds to a chain length equal to 8. The above data show that, the high-temperature reaction of *m*-carborane with aromatic compounds is a degenerative-branched chain process with short chains.

This mechanism explains specific features of carborane-containing polymers behaviour such as decrease in cross-linked reaction temperature and low weight losses, effect of aromatic group introduction and their absence in decomposition products, as well as the absence of proportional dependence between the content of carborane groups in polymer and the effect of decrease in decomposition rate and weight losses. The latter is explained apparently by passing of the cross-linking process competitive with decomposition from a non-chain to a chain process depending on the carborane group content, because unlike other processes (in this case homolytical aromatic substitution) the chain process can ensure the highest cross-linking rates. The *m*-carborane concentration which enables this transformation is determined from expression (8) by life time of the radical adduct and by time required for its collision with a reactive *m*-carborane molecule activated by thermal process. It is interesting to note that *m*-carborane and benzene themselves are high-heat resistant compounds practically stable up to 550°C.[12] Nevertheless, in the presence of carborane-12 the formation of both B-phenyl-*m*-carboranes and diphenyl can be observed at 440°C. The formation of the latter can be explained when amplifying the following reactions to the above scheme:

$$\mathrm{Ar}^{\cdot} + \mathrm{ArH} \underset{k_8}{\overset{k_7}{\rightleftarrows}} \mathrm{Ar_2H}^{\cdot} \tag{9}$$

$$\mathrm{Ar_2H}^{\cdot} + \mathrm{BH} \xrightarrow{k_9} \mathrm{Ar_2H_2} + \mathrm{B}^{\cdot} \tag{10}$$

$$\mathrm{Ar_2H_2} \xrightarrow{k_{10}} \mathrm{Ar_2} + \mathrm{H_2} \tag{11}$$

Then if

$$\frac{d[\mathrm{Ar_2}]}{d\tau} \ll \frac{[\mathrm{ArB}]}{d\tau} \quad \text{and} \quad k_8 \gg k_9[\mathrm{BH}],$$

the ratio between the concentrations of diaryl and B-aryl-*m*-carboranes will be determined by a corresponding experimental (Figure 5) linear relation

$$\frac{d[\mathrm{Ar_2}]}{d[\mathrm{ArB}]} = \frac{K'}{K''}\frac{[\mathrm{ArH}]}{[\mathrm{BH}]}$$

where

$$K = k_9 \cdot \frac{k_7 k_0}{k_1 k_8} \quad \text{and} \quad K = k_4\left(\frac{k_2}{k_3}\right)^{1/2}\left(\frac{k_0}{k_6}\right)^{1/2}$$

This supplement can explain the stabilizing effect of carborane groups with their low content in the polymeric matrix being at high temperatures.

It is known that the processes of thermal oxidation with oxygen proceeds by the fre-radical mechanism. Investigation of oxidation of unsubstituted carboranes-12 showed[8] that at 260–350°C only the products of its deep oxidation and hydrogen are formed. Dimers and higher molecular weight products are not observed in this case. It was established that heating under similar conditions in the presence of aromatic compounds leads to the formation of carborane-12 arylation products. Thus for instance, heating of the *m*-carborane-benzene mixture in the mole ratio 1:2 at 260°C for 1 h gives the following B-phenyl-*m*-carboranes with a

4% yield in %:

2-phenyl-*m*-carborane	16.8
4- and 5- —//—	65.4
9- —//—	17.8

A relative weak strength of the B—H bond[13] we believe to be near to that of the C—H bond in tertiary hydrocarbons (380 kj/mol) must favour easy detachment of hydrogen atom by peroxide radicals in which the strength of the H—OOR bond is 376 ± 8 kj/mol[14] that makes the carborane-12 rather reactive in chain reactions of oxidation. Therefore their intense oxidation observed in the presence of air oxygen at above 200°C is not surprising. At the same time it is known[15,16] that cyclohexadienyl radicals which can be present in oxidation process in the medium of aromatic compounds react with the molecular oxygen to form the hydroperoxide radical. Based on this the oxidative arylation of carboranes-12 can be represented by using the generally accepted scheme of liquid-phase oxidation and adding the above reactions:

$$\mathrm{i} \xrightarrow{k} \mathrm{r}^{\bullet} \tag{12}$$

$$\mathrm{r}^{\bullet} + \mathrm{BH} \xrightarrow{k_0} \mathrm{B}^{\bullet} \tag{13}$$

$$\mathrm{B}^{\bullet} + \mathrm{ArH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArHB}^{\bullet} \tag{14}$$

$$\mathrm{ArHB}^{\bullet} + \mathrm{O}_2 \xrightarrow{k_3} \mathrm{ArB} + \mathrm{HO}_2^{\bullet} \tag{15}$$

$$\mathrm{B}^{\bullet} + \mathrm{O}_2 \xrightarrow{k_4} \mathrm{BO}_2^{\bullet} \tag{16}$$

$$\mathrm{HO}_2^{\bullet} + \mathrm{BH} \xrightarrow{k_5} \mathrm{B}^{\bullet} + \mathrm{H}_2\mathrm{O}_2 \tag{17}$$

An analysis under conditions of degenerative branching and valid relation $k_3[\mathrm{ArHB}^{\bullet}][\mathrm{O}_2] \ll k_5[\mathrm{HO}_2^{\bullet}][\mathrm{BH}]$ shows that the ratio between the arylation and carborane-12 oxidation products does not depend on initiation and termination reactions and is determined by the expression

$$\frac{d[\mathrm{ArB}]}{d[\mathrm{BO}_2^{\bullet}]} = \frac{k_1 k_3 \mathrm{ArH}}{k_4(k_2 + k_3[\mathrm{O}_2])} \approx \frac{k_1[\mathrm{ArH}]}{k_4[\mathrm{O}_2]} \tag{18}$$

It can be expected that the rate constants of carboranyl radical addition to aromatic compounds and oxygen are similar (both reaction are exothermal) and are primarily determined by diffusion. At the same time the concentrations of aromatic groups and oxygen may differ by a factor of hundreds due to low solubility of the latter at high temperatures to assure predominant formation of arylation products observed experimentally. It must be just this fact which explains also the high thermal-oxidative stability of sufficiently bulk samples of carborane-containing polymers. Although in oxidative arylation process the oxygen absorption takes place, the chain stabilization process compensates in this case for thermal-oxidative decomposition of polymeric chains ensure low weight losses.

The results obtained explain as a whole the stabilizing effect of aromatic polymers by carborane-containing additives. It is obvious that this principle of structural-chemical stabilization can be extended into other systems. Essential condition consists in the presence of thermally stable fragments in polymer to assure not only the termination of radical decomposition chain, but also at the same time the formation of new chemical bonds at a rate exceeding the decomposition rate, as observed in arylenecarboranes.

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