STUDY ON THE INITIATION MECHANISM UPON OXIDATION OF METHYLAROMATIC HYDROCARBONS IN PRESENCE OF COBALT ACETATE AND SODIUM BROMIDE IN ACETIC ACID SOLUTION

S.IVANOV and M.HINKOVA

Institute of Organic Chemistry,
Bulgarian Academy of Sciences, Sofia 13, Bulgaria

The initial oxidation stage of methylaromatic hydrocarbons in presence of cobalt acetate tetra-hydrate and sodium bromide has been studied. It has been shown that a direct initiation of the reaction is possible *via* formation of an oxygen complex between cobalt acetate bromide complex and oxygen molecule, which on reaction with hydrocarbon generates free radicals in the oxidizing system. The reaction of oxygen complex with the hydrocarbon is preceded by formation of an intermediate complex, as confirmed by the spectra recorded. The possibility of initiation upon reaction of cobalt acetate bromide complex with hydroperoxides has not been rejected. The highest occupied molecular orbital energies have been calculated after Hukel's method and a correlation is established between these energies and the oxidation rates of methylbenzenes experimentally determined.

As is known, bromine additives used together with catalysts produce a profound accelerating effect upon autoxidation of methylaromatic hydrocarbons with short side chains[1-4]. The kinetics and mechanism of action of the system of bromine activator, catalyst containing transition metal, hydrocarbon and a solvent has been studied by different authors[5-7]. In former works we investigated new types of bromine additives, such as bromides of elements from group *V* of the periodic table[8] and also the effect of various metal atoms when sodium bromide[9] was used as activator.

Present paper studies the effect of the number of methyl groups in benzene nucleus on autoxidation rate in presence of sodium bromide as activator and cobalt acetate as catalyst. The oxidations were carried out in manometric apparatus, analogously to those described in our previous papers[9,10]. For the purpose, we oxidized toluene, *ortho, meta* and *para*-xylenes, 1,2,4-trimethylbenzene, durene, 1,2,4-trimethyl--5-isopropylbenzene and hexamethylbenzene.

EXPERIMENTAL

The hydrocarbons employed were purified. The liquid hydrocarbons were repeatedly treated with sulphuric acid, washed with a mixture of potassium permanganate (2%) and sodium hydroxide (5%), sodium bisulfide and water to neutral reaction, followed by vacuum distillation in an atmosphere of inert gas; the indexes of refraction n_D^{20} of the hydrocarbons purified were following: toluene 1·4963, *o*-xylene 1·5045, *m*-xylene 1·497, *p*-xylene 1·4955, pseudocumene 1·5045, 1,2,4-tri-

methyl-5-isopropylbenzene 1·5065. The solid hydrocarbons were recrystallized from glacial acetic acid: durene, m.p. 91—91·5°C; hexamethylbenzene, m.p. 164—164·5°C. α-Cumyl hydroperoxide, Schuchard Company, was purified using methodics[11], N-phenyl-β-naphthylamine Leba-Chemie-Wien Company, was purified by recrystallization, m.p. 119—120°C (absolute alcohol).
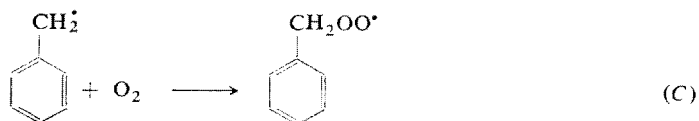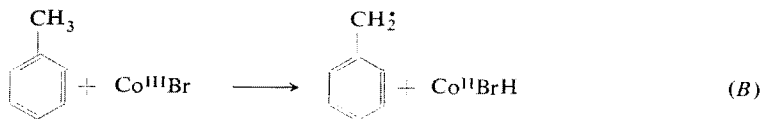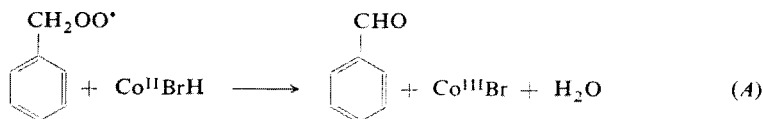
Cobalt acetate with a concentration of $0·75 . 10^{-2}$ mol/l and sodium bromide, $1·5 . 10^{-2}$ mol/l, were added to the solution of the hydrocarbons in acetic acid (4·73 mol/l). After heating on 90°C samples were oxidized in manometric apparatus, and then the amount of oxygen absorbed began to be measured.

RESULTS AND DISCUSSION

The results from oxidation are given in Fig. 1, along with the dependence of oxygen absorbed (calculated in ml) on time. The maximum oxidation rates were determined from the curves.

As presented in the Table I, the initial rate of hydrocarbon oxidation is dependent on the number of methyl groups bonded to the aromatic ring. The rate of oxidation increases with the number of methyl groups. Upon oxidation of xylene isomers, the oxidation rate of p-xylene is the highest. With the rise of number of methyl groups over three, the increase in the rate of oxidation is insignificant. On oxidation of 1,2,4-tri-methyl-5-isopropylbenzene, a sharp increase in rate is observed indicating specific effect of the isopropyl group in the hydrocarbon on the rate of the autocatalytic process in presence of cobalt acetate and sodium bromide.

As known from the data obtained by other authors[4], new chain propagation reactions are assumed to take place upon the oxidation:

$$CH_2OO^{\cdot} + Co^{II}BrH \longrightarrow CHO + Co^{III}Br + H_2O \qquad (A)$$

$$CH_3 + Co^{III}Br \longrightarrow CH_2^{\cdot} + Co^{II}BrH \qquad (B)$$

$$CH_2^{\cdot} + O_2 \longrightarrow CH_2OO^{\cdot} \qquad (C)$$

The same authors have proposed the following rate constant values of reactions (A) and (B) upon toluene oxidation: $k_A = 1$ l/m s, $k_B = 1 . 10^{-2}$ l/m s. The ratio between the rates of reactions (A) and (B) using known concentrations is presented with value $R_A/R_B = 0·85$. As seen from the ratio, the reactions studied take equal part

in the overall rate of oxidation. It is assumed that reaction of initial hydrocarbon with trivalent cobalt occurs in reaction (B). On the other hand, it is known[12] that chain oxidation of aldehydes may readily take place in presence of trivalent cobalt ions. Kamiya and coworkers[4] have established in his work that benzaldehyde consumption

TABLE I

Maximal Rates of Hydrocarbon Oxidation
Conditions of oxidation see Experimental.

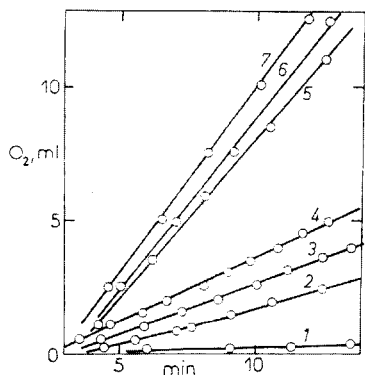| Compound	$R\,10^5$, mol/l s	Compound	$R\,10^5$, mol/l s
Toluene	1·3	Pseudocumene	22·0
o-Xylene	5·9	Durene	22·4
m-Xylene	6·2	Hexamethylbenzene	23·0
p-Xylene	7·2	1,2,4-Trimethyl-5-isopropylbenzene	68·3

FIG. 1

Oxidation of Methylaromatic Hydrocarbons in Acetic Acid Solution in the Presence of $CoAc_2$. $4\,H_2O$ ($0\cdot75$. 10^{-2} mol/l) and NaBr ($1\cdot5$. 10^{-2} mol/l) as Activator and Catalyst, resp. at 90°C and 760 Torr

Hydrocarbons (volume of sample oxidized 5 ml): *1* toluene, *2* o-xylene, *3* m-xylene, *4* p-xylene, *5* pseudocumene, *6* durene, *7* hexamethylbenzene.
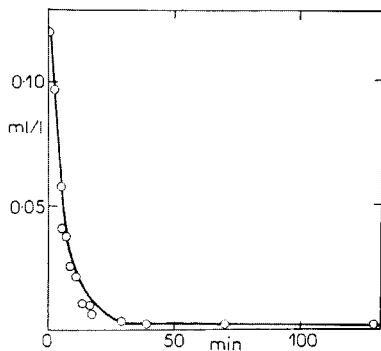

FIG. 2

α-Cumylhydroperoxide Decomposition in $0\cdot2$ mol/l conc. under Action of $CoAc_2$. $4\,H_2O$ ($0\cdot75$. 10^{-2} mol/l) and NaBr ($1\cdot5$. 10^{-2} mol/l)

is not present in the initial stage of toluene oxidation, which shows that it is not oxidized and does not react with cobalt(III). Zakharov and Balanov[5] have suggested a new regeneration reaction of trivalent cobalt ion into divalent, with the aim of avoiding the contradiction

$$Co(III) + Co(II)Br^{(-)} \longrightarrow Co(II) + Co(II)Br^{\cdot} . \qquad (D)$$
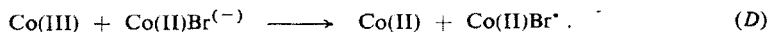
Reaction of cobalt(II) with hydroperoxides is assumed to produce trivalent cobalt.

$$ROOH + Co(III) \longrightarrow R^{\cdot} + Co(III) + HO_2^{(-)} . \qquad (E)$$
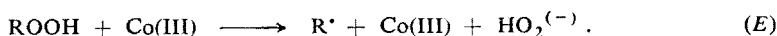
However, from our data it may be concluded (Fig. 1) that maximum oxidation rate is already established in the initial step of oxidation. Before experiments the hydrocarbons were purified using aluminium oxide. Oxygen-containing products, *i.e.* hydroperoxides were thus removed. Therefore, the reaction is directly initiated to maximum rate in the initial step of oxidation, despite of the absence of hydroperoxides. On the other hand, the data obtained by Kamiya reveal that reaction
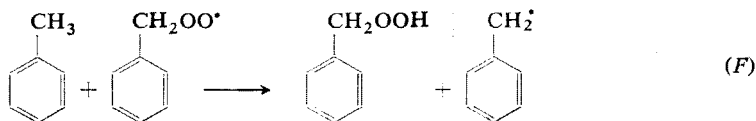
is unsatisfactorily represented in the general scheme of toluene oxidation. R_A/R_F is 425·5, *i.e.* the rate of reaction (A) is higher compared to that of reaction (F) with more than two orders and the formation of hydroperoxide from the total amount of oxygen containing products should not exceed 0·2%. The amount of hydroperoxides obtained during the first 70 minutes of the reaction upon oxygen absorption (5 ml) and toluene oxidated (5 ml) be calculated proceeding from the data obtained in the work and taking into consideration the initial steps of oxidation of methylaromatic hydrocarbons studied in this paper. Under the above mentioned conditions, oxygen containing products with a concentration of $2·2 \cdot 10^{-2}$ mol/l per h are obtained. A total hydroperoxide concentration of $5·2 \cdot 10^{-5}$ mol/l per h would be established for that period of time, according to the calculations above. Obviously, such insignificant amount of hydroperoxide has no substantial effect on initiation of free radicals. This assumption was additionally checked by α-cumyl hydroperoxide decomposition in presence of cobalt acetate $(0·75 \cdot 10^{-2}$ mol/l) and sodium bromide $(1·5 \cdot 10^{-2}$ mol/l); the results are presented on Fig. 2. As seen from the data, the decomposition is accomplished in high rate (initial rate of $2 \cdot 10^{-5}$ mol/l s). The initiating rate calculated is of 10^{-10} mol/l s order. At the same time, value 3·4 .

. 10^{-6} mol/l s is obtained from the actual initiation rate (Fig. 3a) we calculated from the induction periods upon pseudocumene oxidation in presence of N-phenyl--β-naphthylamine.

The results obtained in this work suggest that besides hydroperoxide decomposition forming free radicals in the system and the formation of cobalt(III), the possibility of direct initiation of the reaction *via* formation of an oxygen complex between CoAcBr complex and the oxygen molecule should be assumed as well (this is particularly important for the initial reaction steps):

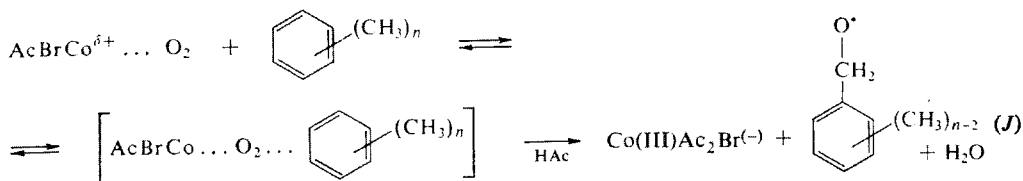$$AcBrCo + O_2 \rightleftharpoons AcBrCo^{\delta+}...O_2^{\delta-} \qquad (G)$$
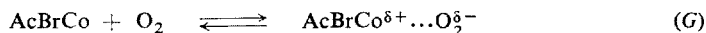
The formation of the complex is favoured by the bromine anion, connected with the cobalt ion, which being a stronger acceptor than the acetic anion will increase the positive charge on cobalt(II). It should be noted here, that similar ideas have already been discussed by Kropf[13] in connection with metal phthallocyanine use in cumene oxidation performed in a liquid phase. Further, the complex thus obtained reacts with a hydrocarbon molecule:

$$(H)$$
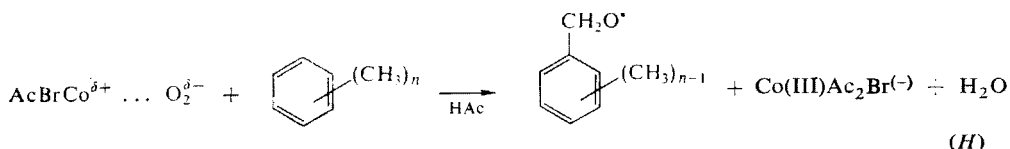
The presence of a similar type reaction suggests effect of hydrocarbon structure on initiation rate, extended further on oxidation rate, *i.e.* a correlation between the number of methyl groups in the methylaromatic hydrocarbon on one hand, and the rate of oxidation, on the other has been assumed. As already mentioned above, similar correlation obtained experimentally may be observed. The results given in Fig. 3b support the interaction. The same figure presents pseudocumene oxidation in presence of cobalt acetate and sodium bromide used as heterogeneous catalyst (*i.e.* only 0·08 ml of acetic acid were added to initiate CoAcBr complex formation). The oxidation proceeds with maximum rate in the initial stage too. It is known that these effects may be observed when heterogeneous catalysts are used in cumene autoxidation in presence of copper phthallocyanine and copper oxide[13,14], and they are interpreted with the presence of a similar type of complex formation.

It may be assumed that reaction (H) proceeds in several stages, *i.e.* the reaction between oxygen complex and hydrocarbon is preceded by formation of an intermediate complex reaction (J):

$$AcBrCo^{\delta+} \ldots O_2 \;+\; \text{(benzene ring)}-(CH_3)_n \;\rightleftharpoons$$

$$\rightleftharpoons \left[AcBrCo \ldots O_2 \ldots \text{(benzene ring)}-(CH_3)_n \right] \xrightarrow[HAc]{} Co(III)Ac_2Br^{(-)} + \text{(benzene ring with } \overset{O^{\cdot}}{CH_2})-(CH_3)_{n-2} \quad (J)$$
$$+ H_2O$$

The possibility of these reactions to occur has been confirmed by the spectra we took of CoAcBr complex in presence and absence of hydrocarbons (Fig. 4). As seen from this figure, deformation in CoAcBr spectrum in the 720 − 640 nm wavelength region in presence of toluene or pseudocumene is observed.

The ideas presented in this paper do not reject the possibility of initiation on reaction of CoAcBr with hydroperoxides. The results obtained by us (Fig. 2) on decomposition of α-cumyl hydroperoxide in presence of the above given complex show that it proceeds at a very high rate. It should be noted that the initial stage of rapid decomposition is followed by a retardation of the decomposition, obviously due to poisoning of the catalyst. Our ideas refer to the initial oxidation stages of methylaromatic hydrocarbons when either no peroxides are detected in the system or their concentration is insignificant, or cases when peroxides are obtained in low amounts due to the nature of the hydrocarbon oxidized. When a hydrocarbon capable of forming hydroperoxides is present, both initiation reactions may occur
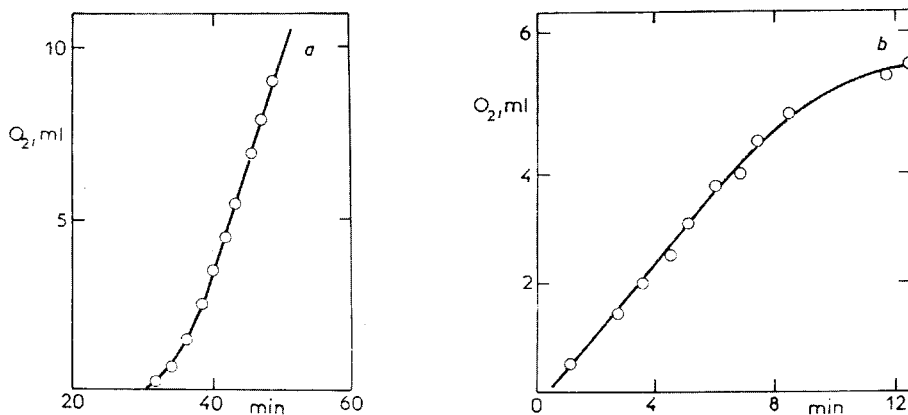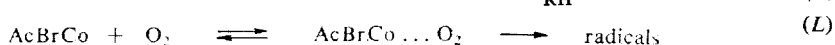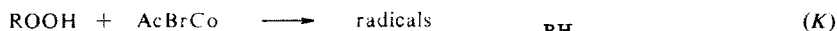

FIG. 3

Pseudocumene Oxidation in Acetic Acid Solution (4·73 mol/l) in Presence of $CoAc_2 . 4 H_2O$ ($0·75 . 10^{-2}$ mol/l) and NaBr ($1·5 . 10^{-2}$ mol/l)

a Oxidation in the presence of N-phenyl-β-naphthylamine ($4 . 10^{-3}$ mol/l); *b* oxidation in heterogeneous phase (CH_3COOH-0·08 ml).

simultaneously, thus producing a strong accelerating effect on the oxidation. This assumption is supported by the fact that 1,2,4-trimethyl-5-isopropylbenzene is oxidized in highest rate. As known, the hydrogen atom bonded to tert-carbon atom in the isopropyl group is readily oxidized forming hydroperoxides.

The competition between the two possible initiation reactions according to contemporary ideas[15] will depend on the electron-acceptor properties of oxygen molecules and the corresponding hydroperoxide in relation to the catalyst studied.

$$ROOH + AcBrCo \longrightarrow radicals \qquad RH \qquad (K)$$

$$AcBrCo + O_2 \rightleftharpoons AcBrCo \ldots O_2 \longrightarrow radicals \qquad (L)$$

The complex formation between CoAcBr and oxygen followed by an interaction with methylaromatic hydrocarbon is in fine correlation with the quantum-chemical calculations of methylbenzene done by us after Hukel's simplified method. The superconjugation referring to the methyl group has been neglected and only the induction effect has been studied. Negative h value has been ascribed to the carbon atom participating in π-system and bonded to the methyl group. In a number of cases this simple model was very useful. It proved quite satisfactory in the case when
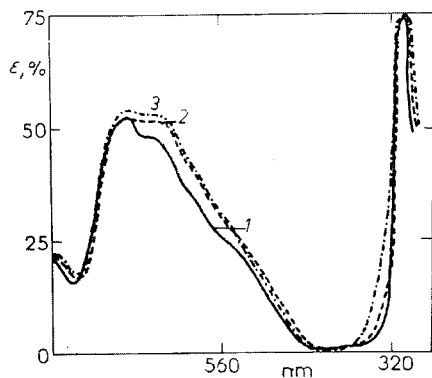

FIG. 4

Spectra of CoAcBr Complex in Acetic Acid [CoAc_2 . 4 H_2O] = 5 . 10^{-2} mol/l, [NaBr] = 1 . 10^{-2} mol/l. 1 CoAcBr complex spectrum, 2 CoAcBr complex spectrum taken in toluene, 3 CoAcBr complex spectrum taken in pseudocumene.
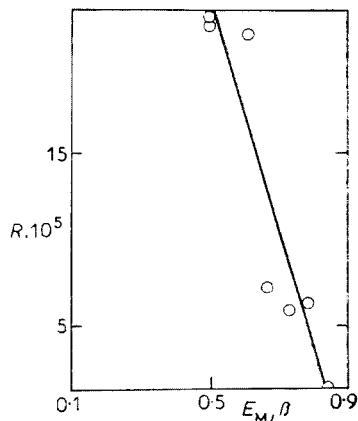
FIG. 5

Dependence of Maximum Oxidation Rate (R, mol/l s) of Methylaromatic Hydrocarbons on Highest Occupied Molecular Orbital Energies

Highest Occupied Molecular Orbital Energies Calculated Theoretically after Hukel's Method

Compound	E_m, β units	I (ref.[23])
Toluene	−0·841	8·82
o-Xylene	−0·727	8·55
m-Xylene	−0·781	8·56
p-Xylene	−0·665	8·447
Pseudocumene	−0·615	8·27
Durene	−0·500	8·03
1,2,4-Trimethylbenzene	−0·437	—
Hexamethylbenzene	−0·500	—

h equaled to -0.5 and was applied for calculating hydrocarbons we used[16] after Hukel's method.

The relationship between the oxidation rate of some compounds and the ionization potential[17,18] is known. The equality between the ionization potential and the highest occupied molecular orbital energy, $I = E_m$, has been proved unambigously in terms of the self-consistent field theory referring to orbital energies calculated according to Hukel's method. This equation is not strictly correct, since the electron interaction is not very accurately recorded. Linear correlation ratios between the ionization potential and the highest occupied molecular orbital energy[19] have been established for some hydrocarbons of the same class:

$$I = a + bE_m . \qquad (1)$$

The literature data[20] referring to ionization potential correlate well with the highest occupied molecular orbital energies (Table II) calculated by us, i.e. Eq. (1) is valid for this case too. In this way, the highest occupied molecular orbital energies could be compared to the oxidation rates determined experimentally. Methylaromatic hydrocarbons studied by us are of the same class. It has been observed that their oxidation rate correlates well with the respective highest occupied molecular orbital energy (Fig. 5).

Compounds with a lower ionization potential have a higher oxidation rate. In this way, the reaction of AcBrCo—O_2 complex with methylated aromatic hydrocarbons assumed by us is confirmed and an intermediate complex formation between oxygen complex and the respective hydrocarbons is suggested. The saturation effect of the rate of oxidation observed with the rise of number of methyl groups in methylaromatic hydrocarbon may be due to the fact that the ionization potential of the molecule is

unaffected upon increase of methyl groups number with more than three, *i.e.* the equilibrium constant between AcBrCo—O_2 complex and the respective polymethyl-benzene does not change further.

REFERENCES

1. Ravens D. A. S.: Trans. Faraday Soc. *55*, 1768 (1959).
2. Kamiya Y.: Tetrahedron *22*, 2029 (1966).
3. Kamiya Y., Nakajima T., Sakoda K.: Bull. Chem. Soc. Japan *39*, 2211 (1966).
4. Sakota K., Kamiya Y., Ohta N.: Bull. Chem. Soc. Japan *41*, 641 (1968).
5. Zacharov I. V., Balanov L. A.: Dokl. Akad. Nauk SSSR *193*, 851 (1970).
6. Digurov H. G., Nastyukova Ja. V., Lebedev N. N., Čerkasova T. H.: Neftechimija *8*, 573 (1968).
7. Ivanov S. K.: Compt. Rend. Acad. Bulg. Sci. *23*, 275 (1970).
8. Ivanov S. K., Shopov D. M.: Compt. Rend. Acad. Bulg. Sci. *24*, 219 (1971).
9. Ivanov C. K., Kateva I.: Com. Dep. Chem. Bulg. Acad. Sci. *5*, 33 (1972).
10. Ivanov C. K., Kateva I.: Compt. Rend. Acad. Bulg. Sci. *21*, 681 (1968).
11. Sergejev P. T., Kružalov B. D.: Chim. Prom. *1957*, 291.
12. Bawn C. E. H.: Discussions Faraday Soc. *14*, 181 (1953).
13. Kropf H.: Ann. *637*, 73, 93, 111 (1960).
14. Jevmenenko N. P., Gorochovatskij Ja. B., Cepalov V. F.: Neftechimija *10*, 226 (1970).
15. Solukvadze L. V., Norikov Ju. D., Naumenko V. I.: Ž. Fiz. Chim. *46*, 3113 (1972).
16. Streitwieser A.: *Molecular Orbital Theory for Organic Chemists*, Russian translation. Izd. Mir, Moscow 1965.
17. Matkovskij K. I.: Dokl. Akad. Nauk SSSR *B5*, 429 (1971).
18. Poluektov V. A.: Dokl. Akad. Nauk SSSR *195*, 889 (1970).
19. Tjutjulkov N.: *Teorija na Molekulnite Orbiti*. Nauka i Izkustvo, Sofia 1970.
20. Vedenejev V. I., Gurvič L. V., Kondratjev V. N., Medvedev V. A., Frankevič E. L.: *Energii Razryva Chimičeskich Svjazej. Potencialy Ionizacii i Srodstvo k Elektronu* (Spravočnik). Izd. Akad. Nauk SSSR, Moscow 1962.