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INFLUENCE OF ELECTRONIC STRUCTURE OF A CATION-RADICAL SKELETON, THE NATURE OF THE ANION ATTACHED TO IT, AND THE NATURE OF THE MEDIUM ON REACTION KINETICS OF ONE-ELECTRON OXIDATION OF TRIPHENYLANTIMONY BY CATION RADICALS OF SUBSTITUTED TRIPHENYLAMINES

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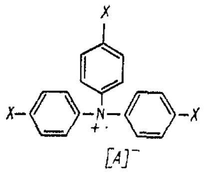
Cation radicals play an important role in the course of various redox processes with the participation of organic substrates [1, 2]. Some stable cation radicals can take part as one-electron oxidants for alcohols [3], substituted benzenes [4], carbazoles [5], free radicals [6-8], and other substrates. As we have already found in [9], the cation radicals of substituted triphenylamines can oxidize triphenyl derivatives of group VA elements by the one-electron transfer mechanism.

In the case of reactions of this type it was interesting to find the factors influencing the reactivity of the cation radicals. In the present work, therefore, we studied by the spectrophotometric method the influence of the electronic structure of the cation-radical skeleton of the radical-oxidant, the nature of the anion attached to it, and the nature of the medium on the kinetic parameters of the oxidation of triphenylantimony (Ph_3Sb) by cation radicals of substituted triphenylamines (I)-(III):



$X = OCH_3$ (I), CH_3 (II), Br (III); $A^- = SbCl_6^-$, BF_4^-, Pi^- = picrate.

The choice of these compounds is due, first, to the fact that cation radicals I-III have high stability and can be isolated as individual compounds in the crystalline state in the form of salts with different anions. These paramagnetic salts are readily soluble in many polar solvents and in media with a low dielectric constant. In organic solvents, in contrast to cation radicals of thianthrene [10] or p-phenylenediamines [11], they are not subjected to disproportionation or dimerization. The reduction of I-III by triphenylantimony proceeds, as will be shown below, in a kinetic region suitable for making measurements, so that this reaction can be used as a model one.

In the reaction of cation radical I hexachloroantimonate with triphenylantimony in $C_2H_4Cl_2$ ($C_0^{I} = 4\cdot10^{-5}$, $C_0^{Ph_3Sb} = 1.2\cdot10^{-3}$ mole/liter) at 20°C, in the visible part of the electronic spectrum a rapid, time-dependent decrease in the absorption band intensity of I ($\lambda_{max}^{I} = 726$ nm) is observed up to its complete disappearance. When antimony pentachloride is added to a solution containing a mixture of the end products of the reaction, the sky-blue

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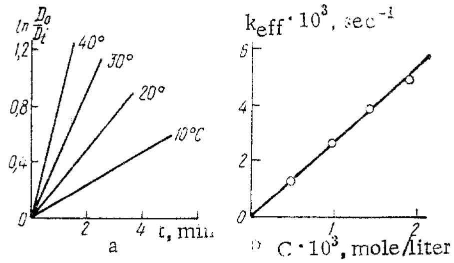


a b

Fig. 1. a) Dependence of ln (D_0/D_t) on t for reduction of cation radical I hexachloroantimonate by triphenylantimony ($C_0^{I} = 4 \cdot 10^{-5}$, $C_0^{Ph_3Sb} = 1.2 \cdot 10^{-3}$ mole/liter; b) dependence of k_{eff} on concentration of triphenylantimony for reaction of cation radical I hexachloroantimonate with Ph_3Sb ($C_0^{I} = 4 \cdot 10^{-5}$ mole/liter).

TABLE 1. Kinetic Parameters of Reaction of Hexachloroantimonates of Cation Radicals I-III with Ph_3Sb in $C_2H_4Cl_2$

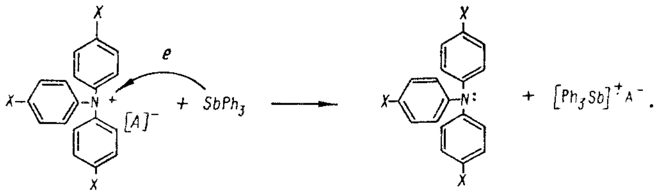
Cation radical	k_2^{30}, liter/mole·sec	E_{act}, kJ/mole
I	3,3	38,1
II	6,5	19,7
III	Reaction proceeds very rapidly	

color characteristic of I is restored, and in the electronic spectrum an absorption band appears with a maximum at 726 nm. Its intensity completely corresponds to that of this band in the initial solution of cation radical I ($C_0^{I} = 4 \cdot 10^{-5}$ mole/liter). Hence in the reaction studied, there occurs a one-electron reduction of the cation radical I by triphenylantimony to the corresponding tri-p-methoxytriphenylamine, and according to the data in [6, 12], its oxidation by $SbCl_5$ leads to the initial cation radical I in a quantitative yield. We have similarly shown that triphenylantimony reduces cation radicals II and III to the corresponding electroneutral amines by the one-electron transfer mechanism.

The study of the reaction kinetics of cation radicals of substituted triphenylamines with Ph_3Sb were carried out spectrophotometrically from the time-dependent changes in the intensity of long-wave absorption bands characteristic of I-III ($\lambda_{max}^{I} = 726$; $\lambda_{max}^{II} = 675$; $\lambda_{max}^{III} = 725$ nm) in the temperature range of 10-40°C.

We found that the rate of the reactions of cation radicals I-III with triphenylantimony is described by a second-order kinetic equation, which includes the concentrations of the cation radical and Ph_3Sb with an exponential factor equal to unity, as follows from the rectilinear course of the dependences in ln (D_0/D_t) vs. t coordinates (D_0 and D_t are the optical densities of the cation radical solution at the initial and current moments of time) and k_{eff} vs. C coordinates (k_{eff} is the effective rate constant; C is the concentration of Ph_3Sb). Figure 1 shows, as an example, the above dependences for cation I.

Spectrophotometric and kinetic studies carried out indicate that the reduction of cation radicals I-III proceeds according to the following scheme:



(1)

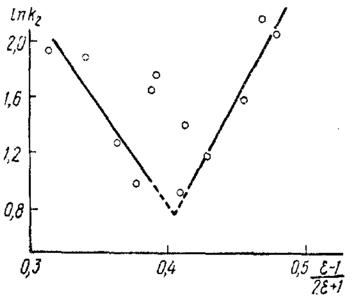


Fig. 2

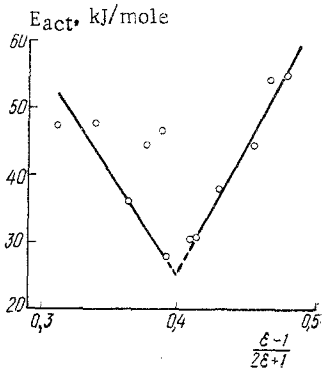


Fig. 3

Fig. 2. Dependence of ln k_2 of reaction of cation radical I hexachloroantimonate on the Kirkwood function at 30°C.

Fig. 3. Dependence of E_{act} on the Kirkwood function for reaction of cation radical hexachloroantimonate with Ph_3Sb in various organic solvents.

The cation radical of triphenylantimony thus formed is apparently an unstable particle which rapidly converts into the subsequent reaction products.

Data in Table 1 show that the rate and energy barrier of the one-electron reduction reaction of cation radicals I-III by triphenylantimony substantially depends on the electronic nature of the substituents in the aromatic ring of the cation radical skeleton. On transition from cation radical I to II, and then to III, the rate of reduction increases due to the decrease in the energy barrier of the reaction. In the case of cation radical III, the reaction proceeds so rapidly that its rate cannot be measured by the procedure used in the present work. The observed change in the reactivity of the cation radicals agrees with their electrochemical characteristics [13], indicating an increase in the electron affinity in the series I < II < III ($E^{I}_{1/2} = 0.56$; $E^{II}_{1/2} = 0.78$; $E^{III}_{1/2} = 1.11$ V; s.c.e. [13]).

Together with the electronic structure of the cation radical skeleton, it was also interesting to clarify the influence of the nature of solvent and the anion attached to the cation radical skeleton, on the kinetic parameters of the process studied, since information on the influence of these factors on the reactivity of not only the cation radicals of substituted triphenylamines I-III, but also on the cation radicals of the other classes is practically unavailable in the literature. Recently, it has been shown [14-16] that depending on the nature of the medium, stable cation radicals of different classes, including those of substituted triphenylamines can be present in the solution, not only as free solvated ions, but also in the form of solvationally separated or contact ion pairs. To find whether there is a difference in the reactivity of free ions and the ion pairs of cation radicals, taking cation radical I hexachloroantimonate as an example, we studied the influence of the nature of solvent on the reduction proceeding by Scheme (1).

In the course of the kinetic studies, the dielectric constant of the medium was varied from 3.5 to 36.0. The kinetic data obtained are shown in Figs. 2 and 3 and in Table 2. Table 2 shows that the nature of the solvent has a noticeable influence on the rate and energy barrier of the one-electron reduction process of I. With decrease in the dielectric constant of the medium, the rate of the reaction decreases, and then increases again, and an unusual V-shaped dependence (Fig. 2) is observed between the logarithm of the rate constant and log $1/\varepsilon$ or the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$, whose minimum is located in the range of the dielectric constant values of the medium [6-8]. A similar V-shaped dependence is also characteristic of the energy barrier values of the reduction of hexachloroantimonate of I by triphenylantimony (Fig. 3). With decrease in the dielectric constant of the medium on transition from CH_3CN ($\varepsilon = 36.0$) to dichloroethane and its mixture with CCl_4, there is a decrease in the activation energy. Then, beginning from $\varepsilon = 8$-6, a further decrease in the dielectric constant of the solvent leads not to a decrease but to an increase in the energy barrier. Since the reduction of the cation radical proceeding by Scheme (1) involves oversolvation of I on transition into the corresponding electroneutral molecule, the de-

TABLE 2. Kinetic Parameters of Reaction of Cation Radical I Hexachloroantimonate with Ph_3Sb in Different Organic Solvents

Solvent	ε	$\frac{\varepsilon-1}{2\varepsilon+1}\cdot 10$	k_2^{30}, liter/ mole · sec	E_{act}, kJ/mole	$-\Delta S$, J/mole · K
$C_2H_4Cl_2+CCl_4$	3,5	3,13	6,9	47,3	81,2
$C_2H_4Cl_2+CCl_4$	4,2	3,40	6,6	47,7	80,4
$CH_3CN+CCl_4$	5,0	3,64	3,6	36,0	123,9
C_6H_5Cl	5,6	3,77	2,7	44,4	98,8
Ethyl acetate	6,2	3,88	5,2	46,5	86,6
$C_2H_4Cl_2+CCl_4$	6,4	3,91	5,8	28,0	146,5
$CH_3CN+CCl_4$	7,7	4,09	2,5	30,6	145,2
$C_2H_4Cl_2+CCl_4$	8,1	4,13	4,1	31,0	139,4
$C_2H_4Cl_2$	10,0	4,29	3,3	38,1	118,0
$CH_3CN+CCl_4$	16,1	4,55	4,9	44,4	93,8
$CH_3CN+CCl_4$	22,3	4,67	8,9	54,0	57,3
CH_3CN	36,0	4,79	7,2	54,8	55,7

crease in the energy barrier of the reaction with decrease in the dielectric constant of the medium (the right-hand branch of the E_{act} vs $(\varepsilon - 1)/(2\varepsilon + 1)$ dependence) can be explained by assuming that the energy required for rearrangement of the solvate shells of I during reduction contributes appreciably to the activation energy of the process studied. Then with decrease in the solvating power of the solvent, the energy barrier of the one-electron reduction reaction of I by triphenylantimony should decrease, which is, in fact, confirmed by the observed dependence (Fig. 3).

On the other hand, as shown in [14-16], the change in the solvating power of the solvent appreciably influences the degree of aggregation of the cation radical salt in the solution. According to [15, 16], on transition from CH_3CN to its mixtures with CCl_4 and mixtures of $C_2H_4Cl_2$ with CCl_4, with decrease in the solvating power of the solvent, the cation radical skeleton associated with the anion into solvationally separated pairs, which predominate in media with $\varepsilon = 8-6$. On further decrease in ε of the solvent, transition of the solvationally separated ion pairs into contact pairs is observed. In the dielectric constant range of the medium of 36.0 to 3.5, the cation radical salt of I is present in the solution in different aggregate states. The data given in Table 1 show that there is a noticeable difference in the reactivity of free ions solvationally separated and contact ion pairs of cation radical I on reduction with triphenylantimony. Since, in accordance with Scheme (1), in reduction a transfer of anion from the triphenylamine cation radical occurs in the transition state, it is natural to expect that the higher the fraction of the contact ion pairs, formed by the cation radical with the anion in the solution, the higher will be the energy barrier of reaction (1). In fact, on further decrease in ε of the medium on transition from solvationally separated pairs into contact pairs, the activation energy of the reduction of cation radical I increases (the left-hand side of the E_{act} vs. $(\varepsilon - 1)/(2\varepsilon + 1)$ dependence). It should be noted that in chlorobenzene and ethyl acetate, the activation energy of reaction (1) is somewhat higher than in other solvents with a comparable dielectric constant. This is apparently due to the possible specific solvation of the cation radical I in these media [16].

Another possible factor influencing the degree of aggregation of cation radical salts is the nature of the anion attached to the cation radical skeleton. In accordance with conductometric and spectrophotometric investigations [14-16], the structure of the ion pair for one and the same cation radical skeleton depends on the charge density on the anions, and hence on the size of the anion. From measurements of Stokes radii of hexachloroantimonate, borofluoride, and picrate anions, carried out in [15], we can arrange them in the following sequence according to increase in the ability to form contact ion pairs: $SbCl_6^- < Pi^- < BF_4^-$.

To clarify the influence of the nature of the anion attached to the cation radical skeleton on the kinetic parameters of the reduction reaction (1), we studied the reaction of cation radical I containing different anions with triphenylantimony. Our studies showed that, as in the case of hexachloroantimonate, the picrate and borofluoride of I are reduced by triphenylantimony to the corresponding tri-p-methoxytriphenylamine, and the rate of these processes obeys a second-order kinetic equation. The kinetic data listed in Table 3 show that the energy barrier of the reaction increases on replacement of the $SbCl_6^-$ anion attached to

TABLE 3. Influence of Anion Attached to Cation Radical Skeleton on Kinetic Parameters of Reaction of Cation Radical I with Ph_3Sb*

Anion	k_2^{30}, liter/mole • sec	E_{act}, kJ/mole
$SbCl_6^-$	5,8	28,0
Pi^-	10,8	41,0
BF_4^-	1,9	54,8

*Solvent — $C_2H_4Cl_2 + CCl_4$; $\varepsilon = 6.4$.

the cation radical skeleton by picrate or borofluoride, which agrees with the above sequence of the ability of the anions to form contact ion pairs.

It must be stressed that in the mixture of dichloroethane with CCl_4 ($\varepsilon = 6.4$), the hexachloroantimonate, picrate, and borofluoride of cation radical I are present in the form of both solvationally separated and contact ion pairs. Therefore, the values of activation energies listed in Table 3 are essentially certain effective values, and cannot be preferentially related to one or another type of ion pairs, since to carry out such a differentiation is at present very difficult.

From the above study it can be concluded that the reactivity of cation radicals, in particular I-III, in redox processes is determined not only by the electronic structure of the cation radical skeleton, but also by the nature of the anion attached to it, and also that of the medium. The results on the influence of solvent lead us to assume that the rate constants and activation energies measured in the case of process (1) actually relate not to the electron transfer stage but to the reorganization processes of the solvate shells of cation radicals and the like.

EXPERIMENTAL

The spectrophotometric and kinetic studies were carried out on a Specord UV-Vis apparatus. Triphenylantimony was synthesized by the method of [17] and purified by recrystallization from petroleum ether. The melting point of Ph_3Sb corresponded to the literature data [17]. Salts of cation radicals I-III containing different anions were prepared by known methods: hexachloroantimonates of I-III according to [12], borofluoride of I according to [18], and picrate of I according to [19], and were recrystallized from a mixture of dichloroethane and diethyl ether (1:5). The purity of the cation radical salts was controlled by their melting points, as well as spectrophotometric and EPR methods. The solvents were purified and dehydrated according to [20].

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