Neutral thallium clusters in aqueous solutions. Pulse radiolysis study

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The formation of neutral Tl_2 (λ_{max} = 390 nm) and Tl_4 (λ_{max} = 360 nm) clusters in dilute aqueous solutions of Tl_2SO_4 containing formate ions was found by pulse radiolysis. The rate constants for the recombination of Tl^0 atoms and Tl_2 clusters are equal to $1.5 \cdot 10^{10}$ L mol^{-1} s^{-1} and $1.0 \cdot 10^{10}$ L mol^{-1} s^{-1} (±30%), respectively, and the extinction coefficient of Tl_2 at 390 nm is ~$6.0 \cdot 10^3$ L mol^{-1} cm^{-1}.

Key words: clusters, radicals, thallium, reduction, absorption spectra, pulse radiolysis.

The primary products of the radiation-induced reduction of Tl^+ ions in aqueous solutions[1–3] are Tl^0 atoms and Tl_2^+ clusters, formed in the reactions

$$e_{aq}^- + Tl^+ \longrightarrow Tl^0 \quad (k = 3 \cdot 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}), \qquad (1)$$

$$Tl^+ + Tl^0 \rightleftharpoons Tl_2^+. \qquad (2)$$

The equilibrium constant for reaction (2) has been reported [1] to be $2.3 \cdot 10^3$ mol L^{-1} or, in another publication,[3] $1.4 \cdot 10^2$ mol L^{-1}. When the initial concentration of Tl^+ ions in solution is high (>$1 \cdot 10^{-2}$ mol L^{-1}), the equilibrium of reaction (2) is shifted to the right and the Tl_2^+ ions are the major products. The optical spectrum of Tl_2^+ exhibits two intense bands at λ_{max} = 420 nm ($\varepsilon = 1.6 \cdot 10^4$ L mol^{-1} cm^{-1})[1–3] and λ_{max} = 245 nm ($\varepsilon = 2.3 \cdot 10^4$ L mol^{-1} cm^{-1})[4] and a low-intensity band at λ_{max} = 700 nm ($\varepsilon = 1.5 \cdot 10^3$ L mol^{-1} cm^{-1}).[4] At a low initial concentration of Tl^+ (<$2 \cdot 10^{-4}$ mol L^{-1}), the equilibrium in reaction (2) is shifted to the left to give mainly Tl^0 atoms, whose optical absorption is characterized by two weak broad bands with λ_{max} = 450 nm ($\varepsilon = 5.0 \cdot 10^3$ L mol^{-1} cm^{-1}) and 260 nm ($\varepsilon = 9.0 \cdot 10^3$ L mol^{-1} cm^{-1}).[4] Recombination of the Tl_2^+ clusters yields positively charged clusters Tl_4^{2+} (a band with λ_{max} = 300 nm).[1]

This study deals with the formation of neutral thallium clusters, which occurs in parallel with the disappearance of Tl^0 atoms in dilute solutions of Tl^+ ions.

Experimental

The pulse radiolysis setup has been described previously.[5] Electrons with an energy of 3.8 MeV were generated using the Van de Graaf accelerator. The pulse duration was 0.1 μs. The optical signals were obtained by averaging the data for ~10 pulses. Variation of the optical absorption was judged based on the extinction coefficient ε, which was determined by dividing the optical density by the concentration of hydrated electrons generated in the pulse. The radiation yield of electrons was taken to be 2.75 species per 100 eV of energy absorbed.

Deaerated aqueous solutions of Tl_2SO_4 containing sodium formate were used. Solutions were prepared using triply distilled water and were saturated with argon.

Results and Discussion

Figure 1 shows the time variation of the absorbance of a solution containing $1 \cdot 10^{-4}$ mol L^{-1} of Tl_2SO_4 and $4 \cdot 10^{-3}$ mol L^{-1} of HCOONa after an electron pulse. Under these conditions, hydrated electrons react with Tl^+ ions (reaction (1)) and the H$^\cdot$ atoms and OH$^\cdot$ radicals react with the HCOO$^-$ ions to give $CO_2^{\cdot -}$ radical ions. The optical spectrum observed after 1 μs contains absorption bands for Tl^0 atoms (λ_{max} 450 nm and 260 nm), which are superimposed on the band of the $CO_2^{\cdot -}$ radical ion (λ_{max} = 235 nm, $\varepsilon = 3.0 \cdot 10^3$ mol L^{-1} cm^{-1}).[6] The atenuation of those bands after several microseconds is accompanied by the appearance of a broad absorption band with a maximum at 390 nm. The overall decay of absorption observed subsequently is accompanied by the appearance, after ~100 μs, of a weak absorption band with a maximum at 360 nm, which can be clearly observed at higher absorbed doses. The decrease in the concentration of Tl_2SO_4 to $5 \cdot 10^{-5}$ mol L^{-1} has no substantial influence on the process. An increase in the dose absorbed per pulse results in a proportional increase in the rate of the decrease in the absorbance at λ_{max} = 450 nm and an increase in the intensity of the band at 390 nm; later, an overall decrease in the absorbance is observed virtually

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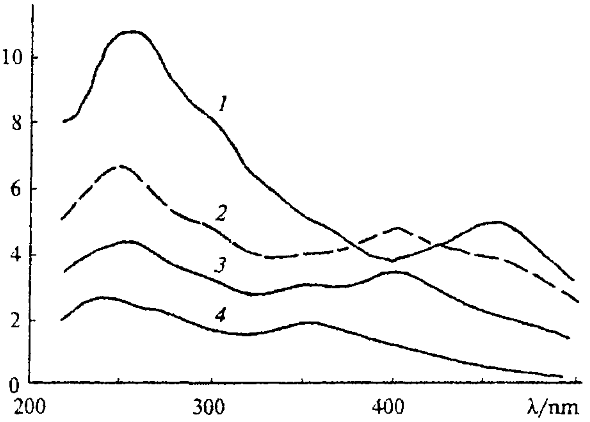

Fig. 1. Optical absorption spectrum of a deaerated solution of Tl_2SO_4 ($1.0 \cdot 10^{-4}$ mol L^{-1}) containing $4.0 \cdot 10^{-3}$ mol L^{-1} of HCOONa 1 (*1*), 12 (*2*), 30 (*3*), and 100 μs (*4*) after the electron pulse. The concentration of hydrated electrons per pulse was $2.0 \cdot 10^{-6}$ mol L^{-1}.

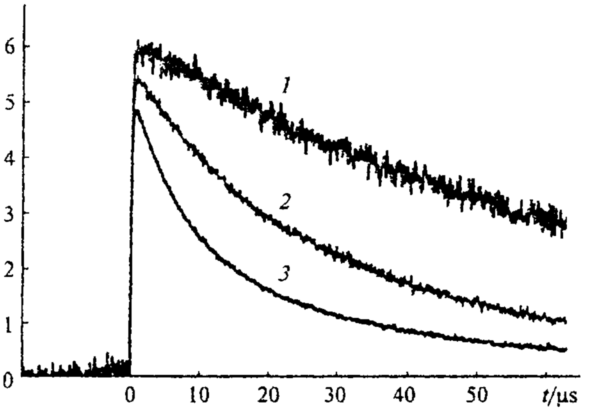

Fig. 2. Kinetic curves for the decay of optical absorption (λ = 350 nm) for various doses absorbed per pulse. The concentrations of hydrated electrons per pulse were $7.3 \cdot 10^{-7}$ (*1*), $2.0 \cdot 10^{-6}$ (*2*), and $5.4 \cdot 10^{-6}$ mol L^{-1} (*3*). The composition of the solution is given in Fig. 1.

over the whole visible and UV region (Fig. 2). This indicates that the variations in the optical spectrum are mainly due to recombination of short-lived species.

Increasing the ionic strength of the solution by adding $NaClO_4$ up to a concentration of 0.5 mol L^{-1} virtually does not change the process kinetics. This implies that the reactions involve neutral species. In our opinion, the bands at 390 and 360 nm are due to electrically neutral thallium clusters, which arise consecutively in the following reactions:

$$Tl^0 + Tl^0 \longrightarrow Tl_2, \quad (3)$$

$$Tl_2 + Tl_2 \longrightarrow Tl_4. \quad (4)$$

Computer simulation of the formation and consumption of noncharged thallium clusters performed using known[7] rate constants for the reactions of the primary products of water radiolysis with one another and with the Tl^+ and $HCOO^-$ ions as well as for reactions (1)—(4) and for the reactions

$$CO_2^{\cdot -} + CO_2^{\cdot -} \longrightarrow (COO^-)_2$$
$$(k = 8.0 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}),^8$$

$$CO_2^{\cdot -} + Tl^+ \longrightarrow CO_2 + Tl^0$$
$$(k = 2.3 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1})^3$$

showed that the best agreement with experimental data is attained for $2k_3 = 3.0 \cdot 10^{10}$ L mol^{-1} s^{-1} and $2k_4 = 2.0 \cdot 10^{10}$ L mol^{-1} s^{-1} (±30%). The extinction coefficient calculated for Tl_2 is ~$6.0 \cdot 10^3$ L mol^{-1} cm^{-1}.

The electrically neutral thallium clusters differ from the positively charged species by their exceptionally high susceptibility for coalescence and by much broader and less intense absorption bands. The same distinctive features have been noted previously for silver clusters.[9] The higher kinetic stability of positively charged clusters is apparently due to the Coulomb repulsion of like charges. The relatively low intensity of the optical bands corresponding to electrically neutral clusters can be attributed to the facts that they contain greater numbers of valence electrons than charged clusters and, correspondingly, that the molecular orbitals are filled to a greater extent and more electron transitions are possible.[10]

The coalescence of thallium clusters results ultimately in the precipitation of metallic Tl. The spectra of thallium sols obtained by radiation-induced chemical reduction of Tl^+ ions in the presence of stabilizing additives are known[11] to exhibit an intense absorption band at 220 nm. These sols are unstable in the absence of a stabilizer and tend to flocculate and coagulate upon addition of electrolytes. Under the conditions of our experiments, the presence of formate ions, apparently, accelerates metal coagulation.

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Addition of carbon-centered radicals to C_{60}. Determination of the rate constants by the spin trap method

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The rate constants of addition of the $^{\cdot}CMe_3$, $^{\cdot}CH_2Me$, $^{\cdot}CH_2(CH_2)_3Me$, $^{\cdot}CH_2Ph$, $^{\cdot}CH_2CH=CH_2$, and $^{\cdot}CH(Me)Et$ radicals to fullerene C_{60} were determined by the method of competitive addition of free radicals to spin traps.

Key words: ESR, fullerene, radicals, spin traps, addition rate constants.

It is known that fullerenes can add various free radicals,[1–3] because of which they are called "radical sponges." Another feature of fullerenes is their high thermal stability, which allows them to be used in studying radical processes[4–5] occurring at 450—500 K, *e.g.*, as radical traps in studies of the kinetics of addition by the method of competitive reactions. Traditional radical traps, nitroso compounds, are unstable and decompose at temperatures ≥350 K. So far the specific use of fullerenes as radical traps has been limited for lack of data on the rate constants of addition of radicals to them. In the present work, the rate constants of addition of carbon-centered benzyl, allyl, and alkyl radicals to fullerene C_{60} were determined by ESR and the method of competitive reactions.[6]

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Samples in glass tubes were degassed by several freezing—evacuating—thawing cycles and irradiated through UFS-2 and KS-15 filters with focused light produced by a DRSh-1000 lamp. Radicals $R^1 = {}^{\cdot}CMe_3$ were generated by photochemical decomposition (λ = 620—680 nm) of Me_3CNO and by elimination of Br atoms from Me_3CBr with $^{\cdot}Re(CO)_5$ radicals,[7] which, in turn, have been obtained by photolysis of $Re_2(CO)_{10}$ under the action of monochromatic UV radiation ($\lambda \approx 366$ nm):

$$Re_2(CO)_{10} \xrightarrow{h\nu} 2\,{}^{\cdot}Re(CO)_5,$$

$$^{\cdot}Re(CO)_5 + BrCMe_3 \longrightarrow {}^{\cdot}CMe_3 + BrRe(CO)_5.$$

By analogy, R^2—R^6 radicals were generated by elimination of Br or I atoms with rhenium-centered radicals: $R^2 = {}^{\cdot}CH_2Me$, $R^3 = {}^{\cdot}CH_2(CH_2)_3Me$, $R^4 = {}^{\cdot}CH_2Ph$, $R^5 = {}^{\cdot}CH_2CH=CH_2$, and $R^6 = {}^{\cdot}CH(Me)Et$. The starting halides and toluene were distilled in an argon atmosphere immediately before use. Radical traps (Sigma) were employed. Time variation of the ESR signal intensities for spin adducts of generated radicals with the traps and C_{60} were least-squares processed in the linear segment (correlation coefficient $R \geq 0.95$).

Results and Discussion

The method of competitive reactions rests on a comparison between the addition rate of free radicals to compounds under study (in this work, to fullerene C_{60}, stage (1)) and to spin traps (**T**) (stage (2)), for which the rate constants of addition of a large number of carbon-centered radicals are known.[6]

$$C_{60} + {}^{\cdot}R \xrightarrow{k_1} {}^{\cdot}C_{60}R, \qquad (1)$$

$$R = R^1\text{—}R^6.$$

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