# The Effect of Tribenzylamine on the Reduction Reaction of the Persulfate Anion

![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

## Abstract

## Full Text

## Physical Chemistry

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# The Effect of Tribenzylamine on the Reduction Reaction of the Persulfate Anion

*(Presented by Academician A. N. Frumkin, 27 VII 1957)*

In recent years a number of authors have established that surface-active organic cations, over the entire range of potentials of their adsorption, increase the rate of reduction of anions ($^1$). The accelerating action of organic cations ceases at sufficiently negative potentials, since large organic cations are displaced from the metal | solution boundary by inorganic cations and water molecules. The increase in the rate of anion reduction can be explained by a decrease in the negative value of the $\psi_1$-potential (the potential at a distance equal to the radius of the reacting particle from the electrode surface), or by a transition of the $\psi_1$-potential from negative values to positive ones ($^{1,2}$).

**Fig. 1.** Polarization curves for the reduction of $10^{-3}N\ K_2S_2O_8 + 10^{-3}N\ H_2SO_4$ with additions of tribenzylamine:
**1** –without additive, **2** –1/100, **3** –1/50, **4** –1/40, **5** –1/30, **6** –1/10, **7** –1/5 of the concentration of a saturated tribenzylamine solution

**Fig. 2.** Polarization curves in a solution of $10^{-3}N\ K_2S_2O_8 + 10^{-3}N\ (C_6H_5CH_2)_3BN$ in the presence of $H_2SO_4$ at concentrations: **1** –$10^{-2}N$, **2** –$10^{-1}N$, **3** –$1N$, **4** –$6N$

As is known from the literature, one of the most effective organic cations is tribenzylamine ($^3$). A. A. Kryukova and M. A. Loshkarev ($^3$), in studying the action of tribenzylamine on the reduction reaction

the anion $S_2O_8^{2-}$ in the presence of $1N$ $H_2SO_4$, however, they observed not acceleration but inhibition of the reduction reaction of the persulfate anion. The authors believe that the action of organic cations cannot be explained by a change in their presence of the $\psi_1$ potential, but is similar to the action of molecular additives that inhibit the reduction reaction of $S_2O_8^{2-}$. However, both

Fig. 3 and Fig. 4 polarographic curves

Figure 3: Fig. 3 and Fig. 4 polarographic curves

the potential range in which inhibition of the reduction reaction was observed and the increase in the reaction rate long before the desorption potential indicate that the inhibitory effect may in this case have another cause.

We studied the action of tribenzylamine on the reduction reaction of the persulfate anion at a dropping mercury electrode.

In dilute background solutions, at potentials more negative than the electrocapillary maximum of mercury, the reduction of $S_2O_8^{2-}$ at the mercury electrode is a slow process, since the approach of the $S_2O_8^{2-}$ anion to the electrode surface is hindered by electrostatic repulsion (4). On the polarographic curve a current drop is observed, which

**Fig. 3.** Polarographic curves in a solution of $10^{-3}N$ $K_2S_2O_8$ + $10^{-3}N$ $(C_6H_5CH_2)_3N$ with additions:
1 –$1N$ $H_2SO_4$, 2 –$1N$ HCl, 3 –$1N$ HBr

**Fig. 4.** Polarographic curves in solutions:
1 –$10^{-3}N$ $K_2S_2O_8$;
2 –$10^{-3}N$ $K_2S_2O_8$+ saturated camphor solution;
3 –$10^{-3}N$ $K_2S_2O_8 + 1N$ $Na_2SO_4$;
4 –$10^{-3}N$ $K_2S_2O_8 + 1N$ $Na_2SO_4$+ saturated camphor solution

disappears at more negative potentials. As is seen from Fig. 1, introduction of tribenzylamine in various concentrations into a solution of $10^{-3}N$ $K_2S_2O_8$ leads to a decrease in the current drop, i.e., to acceleration of the reduction reaction of $S_2O_8^{2-}$ (addition of $10^{-3}N$ $H_2SO_4$ to the solution was necessary, since the solubility of tribenzylamine in neutral and alkaline media is negligible). With increasing concentration of tribenzylamine, an increase of the current at the minimum of the curve is observed. At a tribenzylamine concentration equal to 1/5 of the concentration of a saturated solution, the effect of the current drop disappears completely. Thus, introduction into the solution and adsorption of tribenzylamine, like additions of other organic cations, leads to an increase in the rate of reduction of the persulfate anion.

However, when the concentration of $H_2SO_4$ is increased, inhibition of the reduction reaction of $S_2O_8^{2-}$ by tribenzylamine is observed at the same potentials,

under which it was observed in the work of A. A. Kryukova and M. A. Loshkarev. As is seen from Fig. 2, inhibition of the reaction of reduction of the anion $S_2O_8^{2-}$ is observed when tribenzylamine and the background anion are simultaneously present. The inhibition of the reaction is especially pronounced at potentials more positive than the point of zero charge of mercury, and increases with increasing concentration of the background anions. If the concentration of $H_2SO_4$ is $0.1\,N$, then inhibition of the reaction is observed at $\varphi = -0.5$ V relative to the n.c.e.; if, however, the concentration of $H_2SO_4$ increases to $6N$, then a clearly expressed drop in the current is observed already at the potential $\varphi = -0.8$ V relative to the n.c.e.

An increase in the adsorbability of the background anions also leads to an increase in the inhibition of the reaction of reduction of the persulfate anion by tribenzylamine. Fig. 3 gives the polarization curves for the reduction of the anion $S_2O_8^{2-}$ in the presence of $10^{-3}\,N$ tribenzylamine and $1N$ $H_2SO_4$, HCl, and HBr (the $10^{-3}\,N$ solution of tribenzylamine for all acids was obtained by heating). As is seen from the data presented, the inhibitory effect increases in the series

$$SO_4^{2-} < Cl^- < Br^-.$$

Inhibition of the reaction of reduction of anions during simultaneous adsorption of active anions and organic cations was also observed previously in the action of tetrabutylammonium sulfate on the reduction of $K_2S_2O_8$ in the presence of $1N$ KCl and $1N$ KBr ([5]), and in the action of tetrabutylammonium sulfate and tetrabutylammonium iodide during reduction of the pyrophosphate copper complex ([6]).

The observed effects can be explained in the following way. As follows from electrocapillary measurements, surface-active anions are adsorbed in the presence of active cations, for example tetrapropylammonium, even at negative charges of the surface ([7,2]). Therefore, although organic cations taken separately increase the rate of the reaction of reduction of anions, in the presence of surface-active anions they draw these anions into the surface layer, which leads to inhibition of the reaction of reduction of anions.

In contrast to organic cations, which increase the rate of the reaction of reduction of anions, neutral organic molecules inhibit this reaction ([8,9]). Of the organic additives of molecular character, we chose camphor and a mixture of $\beta$-naphthol, thymol, and diphenylamine as examples of effective additives ([10]). Introduction of a saturated solution of camphor into a $10^{-3}\,N$ solution of $K_2S_2O_8$ leads to strong inhibition of the reaction of reduction of $S_2O_8^{2-}$ (Fig. 4). Desorption of camphor begins at the potential $\varphi = -1.4$ V relative to the n.c.e.; in this case the reaction rate sharply increases and the curve merges with the curve for the pure solution. Thus, inhibition of the reaction by camphor in the region of its adsorption is observed even at low background concentrations (Fig. 4, curve 2). Increasing the background concentration to $1N$ in this case has a different effect than in the case of addition of tribenzylamine (Fig. 4, curve 4). In the potential region from $-0.2$ to $-0.4$ V, a certain increase in inhibition is observed, associated with the salting-out action of the electrolyte with respect to camphor* ([10]). In the region of more negative potentials, camphor causes not an increase but a considerable decrease in inhibition, associated with adsorption of the background cations. The fact that adsorption of the background cation appears already at $\varphi = -0.5$ is connected, apparently, with the fact that camphor shifts the point of zero charge toward positive potentials. An analogous phenomenon was observed in the work of T. V. Kalish and A. N. Frumkin (9). In the case of addition of a mixture of saturated solutions of $\beta$-naphthol, thymol, and diphenylamine, the same phenomena are observed as in the case of addition of camphor. However, the potential region where inhibition is observed is considerably narrower than in the presence of camphor.

* The salting-out action, according to the data of V. V. Losev (10), should be observed in the case of complete saturation of the solution with camphor, which, probably, was not realized in our experiments.

In conclusion, we consider it our pleasant duty to express our gratitude to Academician A. N. Frumkin for his constant guidance and exceptional attention to the work.

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