

On the Electroreduction of Anions

A. N. FRUMKIN AND N. V. NIKOLAJEVA

Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

(Received October 17, 1956)

The electroreduction of anions is often strongly influenced by the electronic charge on the surface of the metallic electrode, and this influence can be traced to the influence of the charge on the composition of the electrical double layer. Experiments cited by others as tending to disprove this supposition are shown to be in fact compatible with it. Neutral molecules containing coordinated chlorine behave with respect to electroreduction much like anions because the chlorine assists in the adsorption of the molecule, and this adsorption is charge sensitive. In all cases the difference in the mechanism of the electroreduction of anions or of neutral particles with anionic groups at different potentials can be interpreted as determined by differences in the conditions of adsorption of the reacting particles.

KIVALO and Laitinen¹ have reported some observations on the electroreduction of anions which they interpret as being in contradiction to a theory of such processes suggested by Frumkin and Florianovich.²⁻⁴ We agree with the experimental results of Kivalo and Laitinen concerning the electroreduction of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ but wish to show that these are not necessarily in opposition to the theory of Frumkin and Florianovich. In the theory of the latter authors an equation was derived which correctly relates the current to the imposed voltage in the reduction of persulfate ion in the presence of KCl of different concentrations. In using the equation no account was taken of the difference between the ψ potentials of the inner and outer

Helmholtz planes. Somewhat earlier a similar relationship had been advanced to explain the phenomena observed during the electroreduction of nitrate ion.⁵

The theory of Frumkin and Florianovich has for its purpose the evaluation of the influence of electrostatic repulsion on the electroreduction of anions, on the assumption that the rate-determining step is the transfer of electrons from the metal to those anions which are in contact with the metal surface. Levich⁶ has evaluated the effect of this repulsion on the somewhat different assumption that the rate of the over-all process is determined by the rate of anion penetration through the electric field of the double layer.

Kivalo and Laitinen report that they were unable to reproduce the minimum in the current-voltage curves of the ferrocyanide electroreduction described by

¹ P. Kivalo and H. Laitinen, *J. Am. Chem. Soc.* **77**, 5205 (1955).

² A. Frumkin and G. Florianovich, *Doklady Akad. Nauk S.S.S.R.* **80**, 907 (1951).

³ G. Florianovich and A. Frumkin, *J. Phys. Chem. (U.S.S.R.)* **29**, 1827 (1955).

⁴ T. Kalish and A. Frumkin, *J. Phys. Chem. (U.S.S.R.)* **28** 473, (1954).

⁵ A. Frumkin, *Actualités sci. et ind.* **373** (1936).

⁶ B. Levich, *Doklady Akad. Nauk S.S.S.R.* **67**, 309 (1949).

Frumkin and Florianovich.⁷ However it appears that Kivalo and Laitinen worked in centinormal solutions of NaOH, and at this ionic concentration the current drop is suppressed.² The minimum in the current-voltage curves for persulfate is also suppressed by inert salts, but a much higher inert salt concentration is required. This explains how it is possible that when two anions (persulfate and ferricyanide) are present simultaneously, the minimum attributable to the reduction of persulfate ion persists after the current drop attributable to the other has been eliminated.

Kivalo and Laitinen propose a new mechanism to explain the current drop in the electroreduction of PtCl_4^{2-} . In brief they assume that mercurous ions are formed by the *chemical* action of PtCl_4^{2-} on mercury and that these mercurous ions serve as a catalyst for the further reduction of PtCl_4^{2-} . Then at a potential of about -0.8 to -1.0 v *vs* S.C.E. the mercurous ions are supposed to fall to so low a concentration that the catalytic effect disappears. It seems inherently unlikely that mercurous ions should exist at sufficient concentrations at, say, -0.7 v to make this mechanism plausible. To test this supposition we have calculated⁸ the potential at which every mercurous ion striking the surface of mercury is immediately reduced. The value obtained is 0.18 v *vs* S.C.E. and is uncertain by one or two tenths of a volt, but not by 1.0 v, which is the difference of potential between this value and that at which the current begins to drop in the electroreduction of PtCl_4^{2-} according to Kivalo and Laitinen.

It was observed by these authors that there is a minimum in the polarogram of the electroreduction of the uncharged molecule $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. We have observed similar minima in the reduction of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2(\text{OH})_2$ but we have not regarded these observations as evidence against the theory of Frumkin and Florianovich because, as was mentioned earlier,^{2,3} the simple mechanism proposed for the reduction of $\text{S}_2\text{O}_8^{2-}$ cannot be applied without modification to anions of the PtCl_4^{2-} type. When PtCl_4^{2-} is reduced on a positively or slightly negatively charged surface of mercury, it is necessary to take into consideration the specific adsorbability of

these ions. Thus modified, the theory can be applied to the electroreduction of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ too. Although this particle is not charged as a whole, its chlorine atoms carry negative charges and their adsorption on the electrode surface is hindered by the growth of the negative charge.

The mechanism of the electroreduction in the region of the second rise of the current-voltage curve and at still higher negative potentials cannot yet be considered as completely elucidated. At one time we were inclined to think that the electroreduction of $\text{S}_2\text{O}_8^{2-}$ in these conditions was made possible by a tunnel effect. However, the marked dependence of the rate of the process on the radius of the cation^{9,10} observed in the case of the electroreduction of $\text{S}_2\text{O}_8^{2-}$ and $\text{S}_4\text{O}_6^{2-}$, suggests rather that the cations in the external Helmholtz layer form bridges that help the anions to approach the negatively charged mercury surface. Under these conditions the equation mentioned above remains applicable if instead of denoting by ψ_1 the mean value of the potential at some distance from the electrode we assume that this quantity represents the local value of the potential at the distance of closest approach to the cations in the Helmholtz layer, as it was already suggested.⁵ In the case of PtCl_4^{2-} or $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, if the process takes place at high negative potentials, a contact between the reacting particle and the electrode surface can probably be effected through the positively charged central Pt atom.

The study of the electrochemical properties of complex compounds is often hampered by chemical reactions into which they enter in aqueous solutions. Along with hydrolysis, to which Kivalo and Laitinen have also drawn attention, it is necessary to take into consideration the reactions of exchange of anionic groups with other electrolytes present in the solution.¹¹

In conclusion we should like to stress that the difference in the mechanism of the electroreduction of anions (or neutral particles with anionic groups) at different potentials can always be interpreted as determined by differences in the conditions of adsorption of the reacting particles, depending on the electrostatic interaction of the reacting particle and the charges of the electrode surface.

⁷ Actually, what Frumkin and Florianovich found was not a minimum in the current, but only a falling off of the current in the neighborhood of the electrocapillary maximum.

⁸ Details of this calculation have been omitted to save space. It depends upon Gerischer and Stauch's evaluation of the mercury-mercurous ion exchange current [*Z. physik. Chem.* **6**, 118 (1956)] and has been corrected for temperature.

⁹ A. Frumkin, *Z. Elektrochem.* **59**, 807 (1955).

¹⁰ I. Zuzula, *Chem. Listy* **47**, 492 (1953).

¹¹ N. Nikolajeva and V. Presniakova, *Doklady Akad. Nauk S.S.S.R.* **87**, 61 (1952).