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POLAROGRAPHIC REDUCTION OF SOME GUANYLPYRAZOLINE NITRATES AND THE EFFECT OF DOUBLE LAYER STRUCTURE ON $E_{1/2}$.

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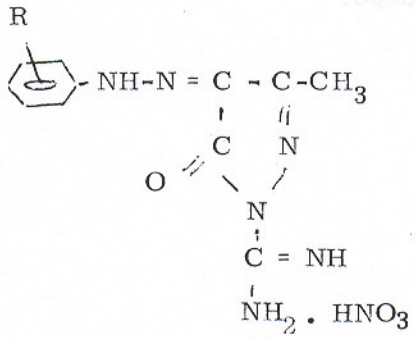
Polarographic reduction of 4-arylhydrazono-1-guanylnitrate-3-methyl-2-pyrazoline-5-ones (I) takes place in a single 4-electron transfer,



(1)

diffusion controlled irreversible wave in B.R. buffers of pH range 2.0 - 10.0. The plots of $E_{1/2}$ vs pH were linear with slopes in the range 45-60 mv/pH. The reduction in these compounds takes place at the -NH-N=C-bond and a plausible mechanism based on the sequence (H^+, e, e, H^+) has been suggested. Effect of supporting electrolyte concentration, various cations and anions and methanol on $E_{1/2}$ has been explained on the basis of double layer structure. The effect of substituents have been interpreted in the terms of Hammett equation. It was interesting

to observe that the nature of cation affects the value of specific reaction constant. The plot of the $(E_{1/2})_H$ - half wave potential of the parent unsubstituted compound - and specific reaction constant in the same supporting electrolyte were found to be linear. It has also been concluded that the reduction process is more susceptible to the substituent effects in presence of larger cations. The positive value of the specific reaction constant ($\rho = 0.17$) indicate a neucleophilic mechanism of the electrode process.