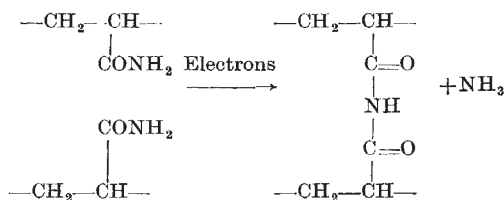
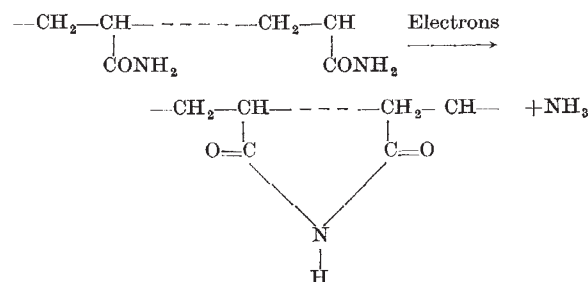


non-irradiated polymer. Softening commenced at $130 \pm 5^\circ \text{C}$ in both cases.

These observations strongly indicate that intermolecular cross-links are formed, on electron irradiation, rather than that the polymer is degraded. It is proposed that the following imidization occurs:



The collapse of single molecules of polyacrylamide in an electron beam may be explained on the basis of intramolecular imidization. The molecules are sprayed from a solvent-precipitant mixture in which the solvent is more volatile than the precipitant. On evaporation, the solvent becomes progressively poor and conditions for polymer-polymer contacts become highly favourable. Spherical, self-supporting molecules can be isolated if the solution is sufficiently dilute. Each molecule consists of a tightly and randomly coiled chain. In this conformation, amide groups along the chain will be in close proximity to one another, and favourable conditions will exist for the condensation of neighbouring amide groups on electron irradiation, as follows:



Further experiments are planned, in an effort to confirm cross-linking. The relationship between irradiation conditions and degree of cross-linking will be investigated from solvent swelling measurements.

Thanks are due to the American Cyanamid Co. for a donation of polyacrylamide.

D. V. QUAYLE

Department of Physics,
Derby and District College of Technology.

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Electron-transfer Reactions of Europium (II) in Aqueous Perchloric Acid Solutions

ELECTRON-TRANSFER reactions with europium (II) as the reducing ion have been studied in aqueous perchloric acid solution, $\mu = 2.0 \text{ M}$, using conventional spectrophotometric techniques. Such reactions are of interest in that little is known about the readiness with which electrons are transferred to and from *f*-orbitals^{1,2}. Although europium (II) is the most stable of lanthanide (II) oxidation states, it reacts rapidly with oxygen and oxygen-free systems have therefore to be used. In preliminary experiments it was shown that europium (II) reduction of perchlorate ions is negligible (europium (II) concentrations of the order 0.04 M).

The reaction



is first order in both the reactants

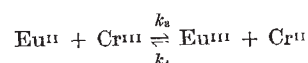
$$\text{Rate} = k_{\text{obs}}[\text{Eu}^{\text{II}}][\text{V}^{\text{III}}]$$

where k_{obs} is hydrogen-ion dependent

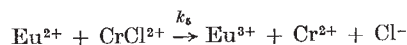
$$k_{\text{obs}} = k_1 + k'[\text{H}^+]^{-1}$$

The rate constant k_1 ($0.0090 \text{ l.mole}^{-1}\text{sec}^{-1}$ at 25°C) corresponds to the reaction of Eu^{2+} with V^{3+} , and it is assumed that k' is for the reaction of Eu^{2+} with VOH^{2+} . Thus k' may be written $k_2 K_H$, where k_2 ($2.00 \text{ l.mole}^{-1}\text{sec}^{-1}$ at 25°C) is the true rate constant and K_H ($0.002 \text{ l.}^{-1}\text{mole}$) (ref. 3) the hydrolysis constant for V^{3+} . From the temperature-dependence activation parameters corresponding to k_1 and k_2 are $\Delta H_1^\ddagger = 11.4 \text{ kcal mole}^{-1}$, $\Delta S_1^\ddagger = -30.1 \text{ e.u.}$, $\Delta H_2^\ddagger = 6.2 \text{ kcal mole}^{-1}$ and $\Delta S_2^\ddagger \sim -35 \text{ e.u.}$ Rates observed for the reaction of chromium (II) with vanadium (III) ($k_{\text{obs}} = 0.85 \text{ l.mole}^{-1}\text{sec}^{-1}$ in 1.0 N, HClO_4 at 25°C , $\mu = 2.0 \text{ M}$) (ref. 4) are considerably faster than those for the europium (II) reaction ($k_{\text{obs}} = 0.013 \text{ l.mole}^{-1}\text{sec}^{-1}$ under identical conditions) although the free energy change is slightly less favourable.

From the difference in standard oxidation potentials of 0.02 volts for the $\text{Eu}^{\text{II}}/\text{Eu}^{\text{III}}$ and $\text{Cr}^{\text{II}}/\text{Cr}^{\text{III}}$ couples⁵ an equilibrium constant of 2.2 can be calculated for the reaction:

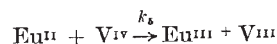


Since the exact nature of the solution medium is important, and the difference in standard oxidation potentials is so very small, such an equilibrium constant can be considered only approximate. Both the forward and reverse reactions have been studied and are extremely slow at 25°C ($k_3 \sim 1.7 \times 10^{-5} \text{ l.mole}^{-1}\text{sec}^{-1}$ and $k_4 \sim 1.4 \times 10^{-5} \text{ l.mole}^{-1}\text{sec}^{-1}$). The addition of chloride ions does not affect the forward reaction, but in the reverse the rate is much faster and substitution inert CrCl^{2+} is formed. With CrCl^{2+} as the chromium (III) reactant the forward reaction is also much faster:



and at 25°C $k_5 = 2.2 \times 10^{-3} \text{ l.mole}^{-1}\text{sec}^{-1}$. A comparison of rate constants for the reactions $\text{Eu}^{2+} - \text{EuCl}^{2+}$ (ref. 6), $\text{Fe}^{2+} - \text{FeCl}^{2+}$ (ref. 7), $\text{Cr}^{2+} - \text{CrCl}^{2+}$ (ref. 8), and $\text{Eu}^{2+} - \text{CrCl}^{2+}$ (which have little or no free energy change) and for the reactions $\text{Cr}^{2+} - \text{Co}(\text{NH}_3)_5 \text{Cl}^{2+}$ and $\text{Eu}^{2+} - \text{Co}(\text{NH}_3)_5 \text{Cl}^{2+}$ (ref. 2) (which have almost identical free energy change) supports the belief that it is more difficult to transfer electrons from *f*-orbitals.

The reaction



is too fast for a full kinetic study using conventional techniques. At 0°C with reactant concentrations $\sim 10^{-4} \text{ M}$ ($\epsilon = 530$ for Eu^{II} at $320 \text{ m}\mu$) and $[\text{H}^+] = 0.2 \text{ N}$, k_6 is $\sim 10^3 \text{ l.mole}^{-1}\text{sec}^{-1}$. In the reactions of europium (II) with chromium (III), vanadium (III), vanadium (IV) and iron (III) (from ref. 9) there is a rough linear correlation of rate constants with the standard free energy change.

A. ADIN

A. G. SYKES

Department of Inorganic and Structural Chemistry,
University of Leeds.

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