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A Preliminary Kinetic Study on the Reaction of Osmium Tetroxide with Thiourea*

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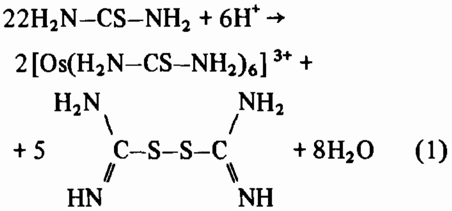
The red complex formed by the reaction of thiourea (tu) with OsO_4 in acid medium used in the classical spectrophotometric determination of Osmium was interpreted according to the scheme [1]



$$2OsO_4 + 22H_2N{-}CS{-}NH_2 + 6H^+ \rightarrow 2[Os(H_2N{-}CS{-}NH_2)_6]^{3+} + 5\,(H_2N)(HN{=})C{-}S{-}S{-}C({=}NH)(NH_2) + 8H_2O \quad (1)$$

Because this reaction is quite slow we have started a kinetic study, in order to point out the best analytical conditions, taking also into account some N-substituted thiourea analogs as N-methylthiourea (me-tu), N,N′-dimethylthiourea (dime-tu) and N,N′-diethylthiourea (diet-tu).

The work conditions were: medium H_2O/EtOH (50:50 Vol); ionic strength: $\mu = 1$ ($HClO_4/NaClO_4$); spectrophotometric measurements in "time-drive" at the wavelength of maxima as follows: $[Os(tu)_6]^{3+}$, $\lambda_{max} = 20800$ cm^{-1}; $[Os(me\text{-}tu)_6]^{3+}$, $\lambda_{max} = 20550$ cm^{-1}; $[Os(dime\text{-}tu)_6]^{3+}$, $\lambda_{max} = 20500$ cm^{-1} and $[Os(diet\text{-}tu)_6]^{3+}$, $\lambda_{max} = 20200$ cm^{-1}.

Each run was conducted under pseudo-first-order conditions with respect to tu and $HClO_4$. The plots of $\ln(A_\infty - A_t)$ against t were straight lines, thus proving the first order with respect to OsO_4.

For $[OsO_4]$ ranging between 6.7×10^{-5} and 2.7×10^{-4} ($[tu] = 10^{-2}$, $[HClO_4] = 1$ and t = 20 °C k_{obs} were independent of the OsO_4 concentration and the value (averaged on 15 runs) was $(1.72 \pm 0.15) \times 10^{-3}$ sec^{-1}.

Working with buffered ionic strength at different values of $HClO_4$ concentration a linear dependence of k_{obs} *versus* $[HClO_4]$ was obtained (see Fig. 1). Therefore, in pseudo-order conditions with respect to thiourea the rate equation is:

$$v = (k'[HClO_4] + k'')[OsO_4]$$

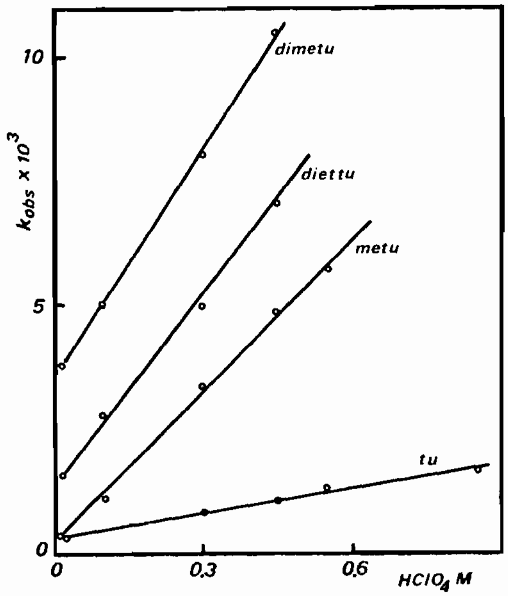


Fig. 1. k_{obs} against the $HClO_4$ concentration. $\mu = 1.0$; t = 20 °C.

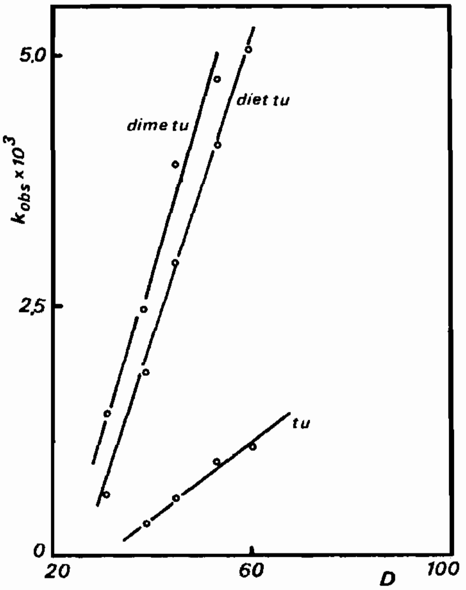


Fig. 2. k_{obs} against the dielectric constant. $\mu = 1.0$; t = 20 °C; H_2O/THF.

By varying the temperature from 20 to 45 °C we determined the thiourea activation parameters* ($E_a = 15.5 \pm 0.4$ Kcal/mol, $\Delta H^{\neq} = 14.9 \pm 0.4$ Kcal/mol and $\Delta S^{\neq} = -20.3 \pm 1.3$ e.u.).

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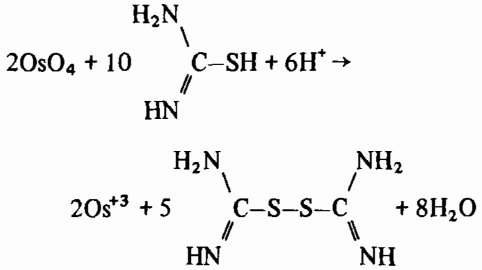
*We intend to obtain the activation parameters for the substituted thioureas by using a more suitable technique like the "stopped-flow".

Furthermore, the k_{obs} were dependent on the dielectric constant of the medium as shown in Fig. 2.

From the experimental data, gathered until now, it is likely to surmise that the rate determining step of reaction (1) is the Red–Ox process in which the Os(VIII) is reduced to Os(III) by the thiourea and the next complexation of Os(III) to $[Os(tu)_6]^{3+}$ is a series of fast steps.

Since the thiolic form of thiourea [2] is responsible for the reduction of Os(VIII) to Os(III) by the reaction



$$2OsO_4 + 10\, \mathrm{H_2N{-}C({=}NH){-}SH} + 6H^+ \rightarrow 2Os^{+3} + 5\, \mathrm{H_2N(HN{=})C{-}S{-}S{-}C({=}NH)NH_2} + 8H_2O \qquad (2)$$

the reactivity can be increased by the factors that lead to the thiolic form, like the addition of mineral acid and the substitution on the N atoms stabilizing the zwitterion form of thioureas [3]. This is confirmed either by the reactivity sequence in agreement with the enhanced basicity of the N-substituted thioureas (tu < me-tu < diet-tu < dime-tu), or by the residual reactivity found when $HClO_4$ is absent; in fact, the relative half-life volumes of dime-tu and diet-tu are 198 sec and 495 sec respectively, much smaller than the tu and me-tu ones (~ 2300 sec).

We have seen how the system reactivity is influenced either by the acid concentration or by the basicity of thioureas; now we would like to investigate the possibility of prereducing the Os(VII) before its reaction with thiourea; in fact, unpublished data show that, on carrying out the reaction in the presence of $SnCl_2$ the red complex forms faster.

References

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