The order of $k_{\text{obs}}$ value is as follows:

(i) For univalent cations (nitrates): $K^+ > Na^+ > NH_4^+$
(ii) For bivalent cations (nitrates): $Ca^{2+} > Sr^{2+} > Mg^{2+} > Ba^{2+}$
(iii) For anions (as potassium salts): $ClO_4^- > NO_3^- > Br^- > CNS^- > I^- > SO_4^{2-} > CH_3COO^- > NO_2^- > H_2PO_4^- > CS(NH_2)_2COO^- > tart^2$

Thanks are due to Dr S. N. Dubey, Principal, Agra College, Agra, for providing necessary facilities and also to UGC for the award of a contingency grant to one of them (M.S.).

References

Kinetics of the Reaction between Ferric Chloride & Thiourea

S. N. Khodaskar & Y. B. Vibhute
Department of Chemistry, Yeshwant Mahavidyalaya
Nanded
and
M. H. Jagdale
Department of Chemistry, Shivaji University, Kolhapur

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Kinetics of the reaction between ferric chloride and thiourea have been studied at pH 1.5. The total order of reaction is found to be 1.5, one with respect to thiourea and 0.5 with respect to ferric chloride. The energy of activation, frequency factor and entropy of activation have been determined. Urea is found as one of the products of the reaction. A probable reaction mechanism has been proposed.

REDOX reactions of ferric chloride in acetone, with some compounds of thiourea type have been reported previously by Kovacovl. However the reaction has not been studied in aqueous medium. The present paper reports the results of a systematic kinetic study of the reaction between ferric chloride and thiourea in water.

All the chemicals used were of CP grade and the solutions were prepared in doubly distilled water. Ferric chloride solution was standardized using Vant Hoff differential equation taking concentration in terms of initial optical density. It is found that the order of reaction with respect to ferric chloride is 0.5. At constant [FeCl$_3$], the rate decreases with increasing [thiourea] (Table 1). The plot of log $k$ against log [thiourea] is linear with a slope of unity indicating that the rate follows first order kinetics with respect to thiourea. Hence the total order of reaction with respect to ferric chloride and thiourea is 1.5.

It is observed that the rate constant increases as the ionic strength increases (Table 3), indicating

![Table 1](image1)

<table>
<thead>
<tr>
<th>M</th>
<th>$-dx/dt \times 10^8$</th>
<th>$[FeCl_3]$</th>
<th>$-dx/dt \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.0</td>
<td>0.0125</td>
<td>6.4</td>
</tr>
<tr>
<td>0.075</td>
<td>8.0</td>
<td>0.005</td>
<td>4.35</td>
</tr>
<tr>
<td>0.025</td>
<td>7.5</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

![Table 2](image2)

<table>
<thead>
<tr>
<th>M</th>
<th>$-dx/dt \times 10^8$</th>
<th>$[FeCl_3]$</th>
<th>$-dx/dt \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.3</td>
<td>1.363</td>
<td>1.69</td>
</tr>
<tr>
<td>0.1</td>
<td>3.0</td>
<td>3.600</td>
<td>4.30</td>
</tr>
<tr>
<td>0.15</td>
<td>6.9</td>
<td>5.710</td>
<td>9.60</td>
</tr>
<tr>
<td>0.20</td>
<td>10.0</td>
<td>10.50</td>
<td>18.0</td>
</tr>
<tr>
<td>0.25</td>
<td>12.4</td>
<td>14.00</td>
<td>28.0</td>
</tr>
</tbody>
</table>

$K_1$ is the first order rate constant and $K_2$ is 1.5 order rate constant.

![Table 3](image3)

<table>
<thead>
<tr>
<th>M</th>
<th>$K_1 \times 10^8$</th>
<th>$[NaCl]$</th>
<th>$K_2 \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.69</td>
<td>0.015</td>
<td>22.0</td>
</tr>
<tr>
<td>0.05</td>
<td>6.6</td>
<td>0.2</td>
<td>24.0</td>
</tr>
</tbody>
</table>

$K_2$ is 1.5 order rate constant.

---

*For correspondence.*
that the reaction is subjected to slight positive salt effect. The course of the reaction has been studied at various temperatures in the range 30-40° and the 1.5 order rate constants have been calculated at different temperatures. The values of energy of activation, frequency factor and entropy of activation are 6.9 ± 0.4 kcal mole⁻¹, 5.78 ± 0.58 x 10⁸ litre mole⁻¹ sec⁻¹ and 62.23 ± 1.5 e.u. respectively. In general when two anions come together to form the activated complex, the resulting entropy of activation is large and negative. From the above data one can postulate an ionic transition state which has extensive charge separation resulting in different temperatures. The values of energy of evaporation of ether layer, white crystals were observed by Behera. He found that the yellow sulphur settles at the bottom. The aqueous layer was analysed for the presence of ferrous or ferric. The presence of ferrous ion was detected by usual semimicro tests. The different stages involved in the reaction may be represented by Eqs. (1-3) and the overall reaction by Eq. (4):

\[
\begin{align*}
\text{(1)} & \quad 2	ext{FeCl}_2 + \frac{1}{2} \text{CS(NH}_2\text{)}_2^+ = \text{Fe}_2 \frac{1}{2} \text{CS(NH}_2\text{)}_2^{2+} + 2\text{Cl}^– \\
\text{(2)} & \quad 2\text{Cl}^– + \text{H}_2\text{O} = 2\text{HCl} + \text{O}^{2–} \\
\text{(3)} & \quad \text{CS(NH}_2\text{)}_2^{2+} + \text{O}^{2–} = \text{CO(NH}_2\text{)}_2^+ + \text{S} \\
\text{(4)} & \quad 2\text{FeCl}_3 + \text{CS(NH}_2\text{)}_2^+ + \text{H}_2\text{O} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S} + \text{CO(NH}_2\text{)}_2^+ \\
\end{align*}
\]

Two of the authors (S.K. and Y.B.V.) are thankful to Shri G. R. Mahasekar, Prinçal, Yeshwant Mahavir‘yadaya, Nanded, for his encouragement and for providing necessary facilities.

References

Molecular Adsorption & Ion Exchange of Carboxylic Acids by Cation-exchange Resin

K. C. Ray*
Department of Chemistry, Visva-Bharati, Santiniketan

L. Pochhali & S. K. Adhikary
Physical Chemistry Laboratory
Department of Chemistry, Jadavpur University
Calcutta 700032

Received 8 December 1976; revised 11 April 1977; accepted 4 May 1977

Molecular adsorption and ion exchange of fatty acids (formic to n-butyric) and mono-, di- and trichloroacetic acids on sodium, potassium and magnesium forms of Amberlite-IR-120 have been studied. The experimental data show that the molecular adsorption increases with the chain length of the hydrocarbon part of the acids for all salt forms of the resin. The sequence of ion exchange for all the salt forms of the resin is propionic < acetic < formic. The position of n-butyric acid is not unique due to the effect of its chain length. For the chloroacetic acids, the sequence of ion exchange is mono- < di- < trichloroacetic and that of adsorption is tri- < di- < monochloroacetic.

Starobinets and Kharevich studied the molecular adsorption of fatty acids on different ionic forms of a cation-exchange resin. But they did not show the simultaneous ion exchange of these acids on the cation-exchange resin, when its counter ions were other than H⁺. Starobinets and Gleim were the first to differentiate between molecular adsorption and ion exchange of weak organic electrolytes on an anion-exchange resin. Ernolenko and Sviricova and Tsitovich and Kuz’menko tried to show the simultaneous molecular adsorption and ion exchange of weak electrolytes using only anion-exchange resins. But no such attempt has been made with a cation-exchange resin. In this paper, differentiation between molecular adsorption and ion exchange of straight chain carboxylic acids (from formic to n-butyric acids) as well as three chloro-substituted acetic acids on Na⁺, K⁺ and Mg²⁺ forms of a strongly acidic cation-exchange resin, Amberlite IR-120, has been presented.

Amberlite IR-120 was converted into H⁺ form by treating with 2N HCl solution. The total exchange capacity of the hydrogen form resin was determined as 4.90 ± 0.04 meq/g of dry resin. The H⁺ form resin was then converted into Na⁺, K⁺ and Mg²⁺ forms.

The experiments were performed at room temperatures (30° ± 2°). Weighed amounts (1 g) of the air-dried resin of known moisture content were mixed with acid (AR) solutions of known initial concentrations in ground stoppered Jena bottles and shaken in a mechanical shaker for 4 hr and then kept for 48 hr to attain equilibrium. After attainment of equilibrium, the acids were estimated by alkalimetric titrations using phenolphthalein indicator. Concentrations of Na⁺ and K⁺ in equilibrium solutions were determined using an EEL flamephotometer with suitable filters for sodium and potassium. The concentration of Mg²⁺ (for magnesium form resin) in the final solution was determined by EDTA titration using Erichrome Black-T indicator. The concentrations of these ions gave the ion-exchange value. The difference between initial and final concentrations gave the total sorption of the acids.

Adsortion as well as ion-exchange isotherms of carboxylic acids are presented in Fig. 1. For all the salt forms of the cation-exchange resin, the molecular adsorption of the carboxylic acids increases in the order, formic < acetic < propionic < n-butyric and for chloroacetic acids the order is, trichloroacetic < dichloroacetic < monochloroacetic. The order of ion exchange for carboxylic acid is n-butyric < propionic < acetic < formic and for chloroacetic acids it is monochloroacetic < dichloroacetic < trichloroacetic. This shows that lower dissociation constants of the carboxylic acids lead to higher adsorption.