An Isotopic Tracer Method for Studying the Mode of Reaction of Sulphur Dioxide on Metal Surfaces

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A n apparatus has been designed to study the corrosion initiation of relatively low concentrations (0.1—1.0 ppm) of sulphur dioxide at room temperature. In order to be able to analyse the corrosion products quantitatively, a $^{35}$S-labelled sulphur dioxide has been used. Preliminary measurements indicate a high percentage of sulphate in the corrosion products.

The corrosion accelerating effect of sulphur dioxide in polluted atmospheres is well-known and has been the subject of many different theories. In the corrosion products from sulphur dioxide adsorbed on metal surfaces, varying amounts of sulphur-containing products with different oxidation states have been detected. The mechanism of the reaction is still not completely clear and further investigation is required.

The apparatus (Fig. 1) consists of a mixing chamber and an oxidation chamber in which the samples are exposed to the sulphur dioxide containing atmosphere and in which the soluble corrosion products are subsequently dissolved. These soluble products are collected in a round flask placed directly under the mixing chamber.

The $^{35}$S- sulphur dioxide was transferred to a steel tube under vacuum and mixed with argon to a pressure of 15 atm. A measured volume of the gas mixture was bubbled through a 1% hydrogen peroxide

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Table 1. Amount of sulphur found on iron samples at 0.5 ppm sulphur dioxide and gasflow 1 l/h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure time</th>
<th>mol analyzed sulphur compounds $\times 10^4$</th>
<th>mol sulphate $\times 10^4$</th>
<th>mol absorbed sulphur dioxide $\times 10^4$</th>
<th>mol sulphur compounds other than sulphate and sulphur dioxide $\times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>7.2</td>
<td>1.4</td>
<td>5.6</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>7.7</td>
<td>2.0</td>
<td>5.6</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>12.8</td>
<td>3.6</td>
<td>8.9</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>13.7</td>
<td>6.1</td>
<td>7.0</td>
<td>0.60</td>
</tr>
</tbody>
</table>

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solution which was titrated with a barium chloride solution using a thorne indicator. The flow rates were measured with flow meters to 1 l/h for air and 0.01 l/h for the sulphur dioxide-argon mixture. The stream of air was allowed to pass through a system of water-containing flasks in order to saturate it with water vapour. Iron samples of high purity were carefully polished chemically and were then exposed to an atmosphere containing 0.1—1.0 ppm sulphur dioxide. The excess of sulphur dioxide was absorbed in a flask containing hydrogen peroxide solution. After an exposure of 5—20 h, the oxidation chamber was filled with 0.1 M hydrochloric acid and the soluble corrosion products were dissolved while a stream of argon was passed through the solution. The solution was then transferred to the round flask where remaining sulphur dioxide, and possibly even hydrogen sulphide, was removed by boiling in vacuo. Samples were taken from the solution and the sulphate was precipitated with barium chloride. The precipitate was analyzed with a Geiger-counter using a sample with known concentration as reference.

The results indicate a high percentage of sulphate in the corrosion products (see Table 1) in agreement with previous experiments. The measured percentages of sulphate can be regarded as constituting the lower limit, since the corrosion products were dissolved under evolution of hydrogen gas, a consequence of the reaction between iron and hydrogen ions. The reproducibility is rather low, probably due to insufficient control of humidity and sulphur dioxide concentration.

Experiments are now being performed under a more rigorous humidity control, and construction materials other than iron are also being investigated.


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Interactions between RNA and DNA at Nucleohistone Formation

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An earlier investigation dealing with the separate behaviour of DNA and RNA at nucleohistone formation in model experiments has now been extended to demonstrate the mutual behaviour of the two nucleic acids when competing for histone.

The principal method used has been described elsewhere. High molecular thymus DNA (Sigma, Type I) and yeast RNA (Sigma, Type XI) were utilized. Thymus histone fractions F₁, F₂, and F₄ were prepared in our laboratory. Stock solutions were made separately of histone and of RNA + DNA mixtures in 0.12 M NaCl buffered to pH 5 with 0.01 M acetic acid-acetate in concentrations of 1 mg/ml. The nucleic acids were mixed in series of reciprocal concentrations from 0.1 mg RNA + 0.9 mg DNA to 0.9 mg RNA + 0.1 DNA (1:9, 1:4, 1:2, 1:1, 3:2, 2:1, 4:1, 9:1; RNA + DNA = 1 mg/ml). Each of these mixtures were in their turn mixed with the F₄ stock solution, in duplicate series of reciprocal concentrations from 0.9 mg nucleic acids + 0.1 mg histone to 0.1 mg nucleic acids + 0.9 mg histone (9:1, 4:1, 7:3, 3:2, 1:1, 2:3, 3:7, 1:4, 1:9; histone + nucleic acids = 1 mg/ml). After 20 min the precipitates formed were centrifuged at 4000 g for 30 min, washed with NaCl buffer and then dissolved in 1 M NaCl. The ultraviolet absorption curves for each precipitate and supernatant were obtained spectrophotometrically using a Unicam automatic scanner. The amounts of histone and nucleic acids were measured through differential readings at two wavelengths. DNA was estimated with the diphenylamine reaction and the amount of RNA was calculated as the difference. One such experimental series is exemplified in Fig. 1. Complementary but less complete series of tests were made for other histones and for ribosomal RNA, s-RNA (Sigma, Type III) and single stranded DNA (Sigma, Type I, heated to +100°C for 10 min and rapidly cooled down). For a reliable comparison of the behaviour of the isolated nucleic acids with their conduct when mutually interacting, the RNA and DNA were further tested.