By Leonard S. Levitt and Edmund R. Malinowski

KINETICS OF PERSULFATE OXIDATION OF ISOPROPYL ALCOHOL

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The kinetics of the persulfate oxidation of isopropyl alcohol were investigated at 60 and 50° in buffered aqueous solution of pH 8.0 and ionic strength 0.5. The rate of disappearance of persulfate was followed by iodometric titration. The reactions all were first order with respect to persulfate. A limiting rate is approached at higher initial alcohol concentrations, and the rate becomes independent of initial alcohol concentration. At lower initial alcohol concentrations of alcohol the rate exhibits a marked decrease and becomes proportional to the alcohol concentration. Thus the reaction is over-all first order at higher alcohol concentrations and over-all second order at lower concentrations. An empirical rate equation relating the observed rate constant to initial alcohol concentration is developed to fit the experimental data. On application of this equation to the data, good agreement between the calculated and experimental rate constants is obtained. An ionic mechanism involving a two-electron transfer, similar to that proposed for the persulfate oxidation of mercaptans and sulfoxides, is presented. From the proposed mechanism a rate equation of the required form is derived: 

\[ -d[S_2O_8^2-]/dt = k_1[S_2O_8^2-][ROH]/[SO_4^{2-}] + k_2[ROH] \]

The common characteristics of many organic oxidations in polar media are discussed.

Experimental

All kinetic runs were made at 60.0°, with an initial concentration of 0.02 M potassium persulfate, an ionic strength of 0.5, and pH 8.0. The samples were titrated iodometrically. The isopropyl alcohol was Eastman Kodak Co. "spectro" grade.

The buffer solution and solution for titration of the samples were prepared in the same manner as previously described, and the experimental procedure also was identical.

Results

In Fig. 1 are presented logarithmic plots of the kinetic data obtained in the oxidation of isopropyl alcohol at initial concentrations of 0.02, 0.01 and 0.005 M. Figure 2 gives similar plots for 0.20, 0.15, 0.10, 0.04, 0.006 and 0.003 M alcohol.

Fig. 1.—Persulfate oxidation of isopropyl alcohol: A, 0.02 M (60°); B, 0.005 M (60°); C, 0.010 M (60°); D, 0.0020 M (two runs, 60°).

Fig. 2.—Persulfate oxidation of isopropyl alcohol at 60°: A, 0.003 M; B, 0.006 M; C, composite of four runs—0.20, 0.15, 0.10 and 0.04 M.

All the reactions are obviously and quite strictly first order with respect to persulfate. There are
points of inflection in the straight lines (Fig. 1) at approximately the concentration for which one would predict, from the stoichiometry of the reaction, that all the alcohol has been oxidized to ketone. The straight-line portion after the break in the curve may be interpreted as the rate of oxidation of the resulting ketone. The rate constant measured for the second portion of these reactions will be designated \( k' \).

Table I gives the rate constants, \( k \), observed for the oxidation of isopropyl alcohol at different initial concentrations. Also included in this table are the corrected rate constants, \( k_c \), obtained by subtracting the value 0.018 hr.\(^{-1} \) (the first-order constant for the disappearance of persulfate when no alcohol is present in the solution\(^2 \)), and the observed and corrected rate constants, \( k \) and \( k_c \), for the portion of reaction after the points of inflection.

### TABLE I

<table>
<thead>
<tr>
<th>Initial concn. of (CH(_3)CH(_2))(_2)OH, M</th>
<th>( k ), hr.(^{-1} )</th>
<th>( k_c ), hr.(^{-1} )</th>
<th>( k' ), hr.(^{-1} )</th>
<th>( k'' ), hr.(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.200</td>
<td>1.07</td>
<td>1.05</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.150</td>
<td>1.07</td>
<td>1.05</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.100</td>
<td>1.07</td>
<td>1.05</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.040</td>
<td>1.05</td>
<td>1.03</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.025</td>
<td>0.90</td>
<td>0.88</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.020</td>
<td>0.85</td>
<td>0.83</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.020</td>
<td>0.83</td>
<td>0.81</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.010</td>
<td>0.73</td>
<td>0.71</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.006</td>
<td>0.55</td>
<td>0.53</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>0.005</td>
<td>0.48</td>
<td>0.46</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>0.003</td>
<td>0.34</td>
<td>0.32</td>
<td>0.11</td>
<td>0.092</td>
</tr>
<tr>
<td>0.018</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>0.000</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

These data are represented graphically in Fig. 3, in which the corrected initial rate constant, \( k_c \), has been plotted vs. the initial alcohol concentration.

![Fig. 3](image)

**Discussion**

It is immediately evident from Fig. 3 that a limiting rate is attained at an initial alcohol concentration of about 0.05 M. Above this concentration the velocity of oxidation is independent of alcohol concentration. At sufficiently low alcohol concentrations the rate exhibits a marked decrease. In this limited range, then, the rate is directly proportional to the concentration of alcohol. Thus the reaction would appear to be over-all second order at alcohol concentrations below 0.05 M and over-all first order at higher concentrations.

**Form of the Rate Equation.**—The following analysis of the data is essentially the same as that given previously\(^3 \) for the persulfate oxidation of mercaptans.

The rate equation may be expressed in the following empirical form

\[
\frac{dP}{dt} = k_cP = k_{max}A_0P/(b + A_0)
\]

in which \( k_c \) is the observed corrected first order rate constant, \( k_{max} \) is the maximum or limiting rate constant, \( b \) is an empirical constant, \( A_0 \), is the initial alcohol concentration, and \( P \) is the persulfate concentration.

Therefore, \( k_c \) is evidently given by

\[
k_c = \frac{k_{max}A_0}{b + A_0}
\]

and the rate is independent of alcohol concentration, and has reached the limiting value. When \( A_0 \ll b \), however

\[
k_c = \frac{k_{max}A_0}{b}
\]

and the rate constant is proportional to the alcohol concentration. At intermediate concentrations, \( k_c \) is always a fraction of \( k_{max} \), the fraction being equal to \( A_0/(b + A_0) \). The constant \( b \) must have the units of concentration, and is, in fact, equal to the alcohol concentration at which the velocity of the reaction has attained one-half its limiting value; for when \( A_0 = b \), then \( k_c = k_{max}A_0/2A_0 = k_{max}/2 \). It may be noted also, from eq. 4, that \( k_{max}/b \) is the slope of the initial straight portion of the plot of \( k_c \) vs. \( A_0 \) (Fig. 3).

**Evaluation of the Empirical Constants.**—Both \( k_{max} \) and \( b \) can be evaluated\(^3 \) more accurately by rearranging eq. 2 to give

\[
\frac{A_0}{k_c} = b/k_{max} + A_0/k_{max}
\]

and plotting \( A_0/k_c \) vs. \( A_0 \), which results in a straight line with slope \( 1/k_{max} \) and intercept \( b/k_{max} \). From such a plot (Fig. 4), the slope is found to be 0.907 and therefore \( k_{max} = 1.10 \); the intercept is equal to \( 6.4 \times 10^{-3} \), and thus \( b = 7.0 \times 10^{-3} \).

![Fig. 4](image)


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*Leonard S. Levitt and Edmund R. Malinowski*
Substituting the numerical values of $k_{\text{max}}$ and $b$ in eq. 2, one obtains

$$k_e = \frac{1.104}{0.0070 + A_0} \quad (6)$$

The observed rate constants, $k_e$, can thus be calculated from eq. 6. Table II gives a comparison of the observed values of $k_e$ at different alcohol concentrations with the values computed from eq. 6. It is seen that the agreement is satisfactory.

| Table II |
|-----------------|-----------------|
| **Observed Rate Constants for the Oxidation of Isopropyl Alcohol and Those Calculated from Equation 6** |
| $k_e$ | Calcul. |
| $A_0$ | (M) | Obsd. |
| 0 | 0 | 0 |
| 0.008 | 0.32 | 0.39 |
| 0.005 | 0.46 | 0.46 |
| 0.006 | 0.55 | 0.51 |
| 0.010 | 0.68 | 0.65 |
| 0.015 | 0.71 | 0.75 |
| 0.020 | 0.82 | 0.83 |
| 0.025 | 0.88 | 0.86 |
| 0.040 | 1.03 | 0.94 |
| 0.100 | 1.05 | 1.03 |
| 0.150 | 1.05 | 1.05 |
| 0.200 | 1.05 | 1.06 |

**Activation Energy.**—A kinetic run was made at 50.0°C with a 0.02 M initial concentration of each of the reactants (Fig. 1). The rate constant ($k_e$) was 0.23 from which, together with the average value 0.82 observed at 60.0°C, one obtains a value of 26 kcal./mole for the energy of activation. This may be compared with the following values observed in other persulfate oxidations: mercaptans, 26 kcal.; sulfoxides, 25 kcal.; and water, 32 kcal.

**Proposed Mechanism.**—The relatively high activation energies observed in all these oxidations afford evidence that the reactions are not of the radical-chain type. In addition, molecular oxygen has no effect on the rate of the persulfate oxidation of diethyl sulfoxide or of toluene.

The nature of the rate dependence upon initial alcohol concentration suggests a mechanism involving one or more equilibrium steps and a rate-determining one. A mechanism for these reactions should also account for the retarding effect that sulfur ion has on the rate.

The following mechanism, substantially in agreement with these requirements, is essentially the same as that postulated for the oxidation of sulfoxides, mercaptans and of water by persulfate.

\[
\begin{align*}
O_3^+ + O_3^- & \rightleftharpoons O_5^+ \quad (7) \\
R\text{C} + O_3^- & \rightleftharpoons R\text{C}O_3^- \quad (8) \\
R\text{C}O_3^- + O_3^- & \rightleftharpoons R\text{C}O_3^2^- \quad (9)
\end{align*}
\]

It is assumed (eq. 7) that the persulfate ion dissociates by means of a heterolytic cleavage, into a sulfate ion and a molecule of sulfur tetroxide (SO$_4^-$), which is here considered to be the active oxidizing species. The electron deficient sulfur tetroxide then attacks the lone electron pair of the oxygen atom of the alcohol to form, reversibly, a monopersulfate ester (eq. 8). Subsequent heterolytic decomposition gives rise to the reaction products (eq. 9).

The constant $k_{-1}$ must be quite small since radioactive sulfate exchanges with persulfate very slowly. Free sulfur tetroxide, which is a powerful oxidizing agent, has been prepared. It is thought to be the anhydride of monopersulfuric (Caro's) acid (H$_2$SO$_5$), but reacts only slowly with water.

**Derivation of the Rate Equation.**—From the foregoing mechanism, a rate equation of the required form (cf. eq. 1) may be derived in the following manner.

Since the limiting rate which is reached in these oxidations is a much lower limiting rate than that observed in the persulfate oxidation of mercaptans at the same temperature (calculated from the activation energy), one of the rate constants in the forward direction, other than $k_1$, must be small; for if $k_1$ were the only slow and rate-determining reaction, then the same limiting rate should be observed in the oxidation of alcohols, sulfoxides, mercaptans and, in fact, any oxidizable substrate present. Hence it will be assumed that the decomposition of the ester ($k_5$) is a slow reaction with a rate of the same order of magnitude as $k_1$. In such a case, the intermediate complex (ester) can accumulate to a considerable extent, and an equilibrium (rather than a steady state) treatment is applicable.

The concentration of the ester will be represented as $[X]$ and the equilibrium constants for eq. 7 and 8 are designated, respectively, $K_1$ and $K_2$. Thus

\[
K_1 = k_1/k_{-1} = [SO_4^-]/[SO_3^-] \quad (10)
\]

and

\[
K_2 = k_5/k_{-5} = [X]/[SO_4^-] \quad (11)
\]

Equation 11 permits the concentration of the complex to be calculated in terms of the concentration of sulfur tetroxide and of alcohol. These concentrations, however, will not correspond to the initial concentrations, since appreciable amounts will have reacted to form the complex. Therefore, [SO$_4^-$] should be replaced by [SO$_4^-$] $-$ [X], and [ROH] by [ROH] $-$ [X] (where the subscript zero refers to the initial concentration).

Equation 11 then becomes

\[
K_2 = [X]/([ROH] - [X]) [SO_4^-] \quad (12)
\]

This quadratic in $[X]$ can be simplified by assuming

\[
\]


that $[ROH] \gg [SO_2]$; then, since $[X]$ cannot exceed $[SO_2]$, it is negligible compared to $[ROH]$, but not negligible in comparison to $[SO_2]$. With this simplification eq. 12 may be written

$$K_2 = \frac{[X]/[ROH]}{[SO_2]/[ROH] + K - 1}$$

from which $[X]$ is given by

$$[X] = K_2[ROH]_0[SO_2]/(K_2[ROH]_0 + K - 1)$$

Substituting in eq. 14 the equivalent of $[SO_2]$ given by eq. 10, and setting the over-all rate equal to $kX$, one obtains the final rate expression

$$\frac{d[SO_2]_0}{dt} = kK_2[ROH]_0[SO_2]/([SO_2]_0/K_2 + [ROH]_0)$$

It is seen that this equation is of the same form as the empirical expression (eq. 1), and that therefore

$$k_{\text{max}} = kK_2[SO_2]$$

and

$$b = K - 1 = 1/K_2$$

Thus the equilibrium constant $K_2$ for the formation of the ester $X$ may be calculated from eq. 17. For isopropyl alcohol at $60^\circ$, $K_2 = 1/7.0 \times 10^{-1} = 1.4 \times 10^{-1}$.

From eq. 16, the product $kK_2$ can evidently be evaluated, but the rate constant $k$ and the equilibrium constant $K_2$ cannot be individually calculated from the data obtained in this investigation.

The Common Characteristics of Organic Oxidations in Polar Solution.—The mechanism postulated here for the persulfate oxidation of a secondary alcohol seems quite possibly to be the general mechanism by which alcohols (and perhaps many other organic compounds) are oxidized in polar media by the common strong inorganic oxidizing agents. The mechanistic courses of these reactions appear almost always to possess in common the following characteristics.

1. The active oxidizing species is rarely, if ever, a negative ion (e.g., $NO_2^-$, $CrO_4^{2-}$, $SO_2O_4^{2-}$, $ClO^-$, $IO_2^-$), but appears to be most usually an electron deficient cationic species (e.g., $NO_3^+$, $CrO_3H^+$, $IO_3^-$, $HCl$) or a highly polar molecule (e.g., $NO_2$, $CrO_2H$, $SO_2O_4$) capable of undergoing a simple two-electron transfer (e.g., $NO_2 \rightarrow NO_2^-$; $CrO_2H \rightarrow CrO_2H^-$; $SO_2O_4 \rightarrow SO_2O_4^-$; $ClO^+ \rightarrow Cl$; $IO_3^- \rightarrow IO_3^-$). These electrophilic substances are generally identical with those responsible for ordinary aromatic substitutions.

2. The positively charged atom of the active oxidizing species initially attacks a free electron pair of the reactant at a relatively electronegative site (e.g., $-O_2^-, -S^-, -X^-, =N^-$) forming a coordinate bond. The atom attacked gains a positive charge.

3. The positive charge is removed by expulsion of a positive fragment (usually $H^+$) or by combination with a readily available anion.

4. The oxidant begins to move off with the electron pair of the coordinate bond, resulting in a transition state in which an incipiently forming positive organic species simultaneously expels a second positive fragment or combines with a second negative ion.

All the common oxidizing agents are much more powerful in strongly acidic solutions principally, it seems, because of the ease with which the active oxidizing species are formed in the presence of a proton donor by reactions typified by the following examples:

$$2HNO_3 \rightarrow NO_3^- + H^+ + H_2O \rightarrow H_2O + NO_2$$

$$2HCl \rightarrow Cl^- + H_2O \rightarrow H_2O - Cl^-$$

$$H^+ + HCl \rightarrow Cl^- + H_2O \rightarrow H_2O - Cl^-$$

$$2H^+ + MnO_4^- \rightarrow MnO_2 \rightarrow H_2O + MnO_2$$

$$3H^+ + CrO_2^+ \rightarrow CrO_2H \rightarrow H_2O + CrO_2H$$

The four characteristics outlined above provide the common basis of many oxidation mechanisms previously proposed, such as the oxidation of mercaptans and sulfoxides by persulfate; the chromic acid oxidation of secondary alcohols; the oxidation of alcohols and of formic acid by hypochlorous acid; and the oxidation of sulfides by acidic hydrogen peroxide. One example, the hypochlorous acid oxidation of primary alcohols, will suffice for illustrative purposes. This reaction apparently proceeds through the intermediate formation of the hypochlorite ester in the following manner:

$$H^+ + HOCl \rightarrow HOCl \rightarrow H_2O + Cl^-$$

$$RCH_2OH + HOCl \rightarrow RCH_2OCl + Cl^-$$

These oxidations are first order in HOCl and alcohol and are accelerated by $H^+$ ion, because of the initial equilibrium in which $Cl^+$ is formed. An example of the oxidative cleavage of a tertiary alcohol is the nitric acid oxidation of 1-phenylcyclohexanol, which almost certainly proceeds by way of the nitrate ester in the following manner:

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NO}_2$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{NO}_2 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^+$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^+ + \text{CI}^- \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^-$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{CI}^+ \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$$

$$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$$
Further oxidation of the keto alcohol results in the final product, \( \text{C}_8\text{H}_7\text{COO}(\text{CH}_2)_3\text{COOH} \). The reaction of carbonyl groups with oxidizing agents, such as chromic acid or potassium permanganate, is a typical example. For analytical purposes, tungsten carbide powder is known to burn in air, and the reaction appears to go through an intermediate stage of ester formation. For example, when \( \text{Cr}_2\text{O}_3 \), \( \text{HNO}_3 \), or \( \text{HClO}_4 \) is the oxidizing agent, the ester formed is \( \text{RCHO} \). This ester can expel only a carbonium ion (\( \text{R}^+ \)) from \( \text{R}: \text{C} - \text{O}^- \), whereas a tertiary ester can expel only a carbonium ion (\( \text{R}^+ \)) from \( \text{R}: \text{C} - \text{O}^- \), which is, energetically, more difficult to do. Thus, \( \text{t-butyl hypochlorite} \) and \( \text{chromate} \) are surprisingly stable.

The formation of carboxylic acids in the oxidative cleavage of tertiary esters, ketones, and acids is implicit in the generalized approach to organic oxidation presented here. Even primary and secondary alcohols might-be expected to expel carbonium ions in competition with proton ejection when the carbonium ion (such as \( \text{CH}_3\text{C}^+ \) or \( \text{C}_8\text{H}_7\text{C}^+ \)) is one that can be formed readily because of its relative stability. Such cleavage actually has been observed in the case of the chromic acid oxidation of methyl-\( t\)-butylcarbinol to \( t\)-butyl alcohol and acetaldehyde and of phenyl-\( t\)-butyl-carbinol to \( t\)-butyl alcohol and benzaldehyde. The mechanism of the cleavage is easily explained on the basis of the present view, and may be simply represented as

\[
\text{RCH}_2\text{C}^+ \rightarrow \text{RCH}_2\text{C}^- + \text{H}^+
\]

If carboxylic acids of sufficiently long half-life are actually ejected from molecules undergoing oxidative fission of \( \text{C} - \text{C} \) bonds, one might expect that rearrangements involving certain of them would have been noted. Such molecular rearrangements have in fact been observed, for example in the chromic acid oxidation of cyclooctatetraene to \( \text{p} \)-benzoic acid, and in the permanganate oxidation of camphene to camphoric acid. Both of these reactions may be explained readily on the basis outlined here.

\[
(\text{CH}_3)_2\text{C}:\text{CH}^+ \rightarrow (\text{CH}_3)_2\text{CO}^- + \text{H}^+
\]

The curves from four experiments are shown in air at 500 to 520°, and can be burned completely at 520°.

The materials used were: (1) a tungsten carbide powder supplied by the Carbolyx Department of the General Electric Company. This material contained 6.24 ± 0.04% C, or 0.11% more than theoretical. (2) A macrocrystalline tungsten carbide obtained from the Wah Chang Corporation. Samples of these materials were weighed into porcelain crucibles and heated at a rate of 300°/hr. (unless otherwise noted) in a pen-recording Chevenard thermo-balance. This instrument, manufactured by Société Adamel, is similar in principle and operation to that described by Duval.

The curves from four experiments are shown in

\[
(\text{CH}_3)_2\text{C}:\text{CH}^+ \rightarrow (\text{CH}_3)_2\text{CO}^- + \text{H}^+
\]

NOTES

**The Oxidation of Tungsten Carbide**

**By Arthur E. Newkirk**

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Tungsten carbide powder is known to burn in air, but information about the ignition temperature and rate of combustion seems lacking. For analytical combustion it is common to use high temperatures, oxygen and a flux, although rapid direct combustion can be achieved at approximately 1400° in oxygen. The present thermobalance studies show that fine tungsten carbide powder begins to oxidize rapidly in air at 500 to 520°, and can be burned completely at 520°.

The materials used were: (1) a tungsten carbide powder supplied by the Carbolyx Department of the General Electric Company. This material contained 6.24 ± 0.04% C, or 0.11% more than theoretical. (2) A macrocrystalline tungsten carbide obtained from the Wah Chang Corporation. Samples of these materials were weighed into porcelain crucibles and heated at a rate of 300°/hr. (unless otherwise noted) in a pen-recording Chevenard thermo-balance. This instrument, manufactured by Société Adamel, is similar in principle and operation to that described by Duval.

The curves from four experiments are shown in