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# DETERMINATION OF OXIDATIVE STABILITY OF ROSIN PRODUCTS BY HIGH-PRESSURE DIFFERENTIAL SCANNING CALORIMETRY

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## ABSTRACT

High-pressure differential scanning calorimetry (HPDSC) was used to determine the oxidative stability of various rosins and rosin products. Gum rosin was considerably more stable to oxidation than were wood rosin and tall oil rosin, suggesting the presence of more natural antioxidant in gum rosin. Hydrogenation, polymerization and disproportionation of rosin all resulted in increased oxidative stability, presumably due to the decrease in conjugated double-bond structures typical of abietic acid-type molecules. Esterification of rosin with glycerol or with pentaerythritol also increased oxidative stability. HPDSC exotherms were also determined for six purified rosin acid structures including abietic, neoabietic, palustric, levopimaric, isopimaric and dehydroabietic acid. Dehydroabietic acid was far more stable to oxidation than the others. In general, the HPDSC results fit the picture that an allylic H atom is oxidized much faster than a nonallylic H atom, and that two conjugated double bonds result in extreme activation.

## INTRODUCTION

It is well known that oxidation is one of the main reactions leading to rosin deterioration, and it is one of the major factors in color formation [1]. Although there are various schemes for determining the amount of $O_2$ taken up by a substance in a designated period of time, one of the more recent methods of determining the susceptibility of a substance to oxidation is high pressure differential scanning calorimetry (HPDSC). In this technique, a sample is subjected to oxidation in a controlled isothermal system under $O_2$ pressure, and the amount of time necessary to reach the oxidation exotherm is measured.

In 1971, Noel reported the use of HPDSC in determining oxidative stabilities of lubricating oils [2]. Later, the technique was used at the National Bureau of Standards in examining stabilities of oil basestocks [3]. In addition, oxidative stabilities of fatty acid methyl esters and triglycerides were studied by HPDSC at the National Food Research Institute in Japan [4].

In the present work, the HPDSC method developed by Dugan and McCarty [5] was used to analyze a number of rosin products (including six purified resin acids structures), and the relationship between structure and susceptibility to oxidation is described.

## EXPERIMENTAL

HPDSC was carried out using a DuPont high-pressure DSC cell (Model 900830-902) in conjunction with an Omnitherm QC-25 thermal analyzer and a Houston recorder (Model B5117-1). Indium was used to calibrate the thermal analyzer.

Using 5–7-mg samples, HPDSC values were determined at an oxygen pressure of 550 psi (Tables 1–3, Figs. 1–3). Isothermal conditions were chosen to provide a reasonable exotherm time. Within the designated range, sample weight was not important and, in most cases, the sample was not weighed. Exotherm time was measured from the start of the run to the maximum of the exotherm peak.

In choosing a sample for analysis, it was important to obtain a sample which had not been exposed to air oxidation. Surface samples and fines were avoided, and the sample was taken from the interior of a chunk of the rosin. The sample was placed in a small aluminium pan with an empty pan serving as reference standard.

Reproducibility was usually ±10% of the obtained value. Wider variations were traced to sample nonhomogeneity. Because solid rosin samples are reasonably homogeneous (with the exception of exposed surfaces), HPDSC can be used successfully.

As can be seen in Table 2, with the disproportionated rosin sample determinations, a change in temperature of 10°C corresponded to about a two-fold change in reaction rate. Simple regression analysis of the HPDSC data showed an $R^2 > 0.99$ for such a relationship. Because of this correspondence it was possible to convert all HPDSC values to 100°C for comparison.

The pale wood rosin and all of the rosin derivatives were obtained from the Hercules plant at Hattiesburg, Mississippi. Tall oil rosin (TOR) was a

TABLE 1

HPDSC of various rosins

| | Temp. (°C) | HPDSC exotherm (min) |
|---|---|---|
| Pale wood rosin | 100 | 11 |
| Pale wood rosin fines | 100 | 6 |
| Tall oil rosin | 100 | 13 |
| Gum rosin | 100 | 30 |

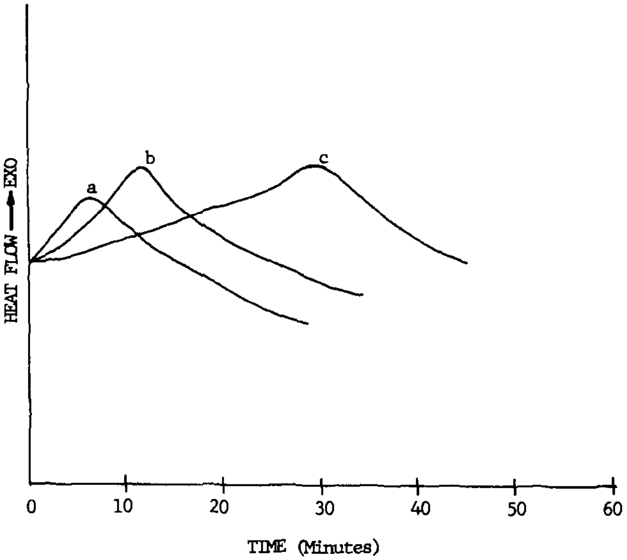


Fig. 1. HPDSC of rosins at 550 psi $O_2$ and 100°C. (a) Pale wood rosin fines, (b) pale wood rosin, (c) gum rosin.

typical side-stream TOR, and the gum rosin was Chinese gum rosin. Purified resin acids were supplied by B.C. Research, Vancouver, Canada. In HPLC analysis, dehydroabietic acid, neoabietic acid, levopimaric acid and isopimaric acid exhibited only one peak. Palustric acid contained one extra

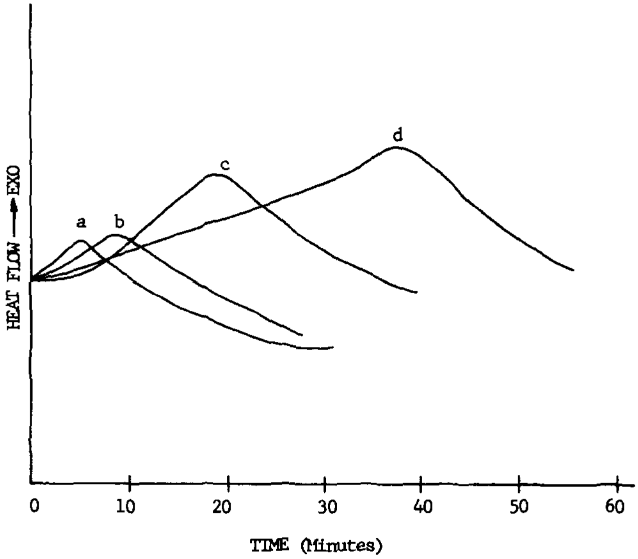


Fig. 2. HPDSC of disproportionated rosin at 550 psi $O_2$. (a) 160, (b) 150, (c) 140, (d) 130°C.

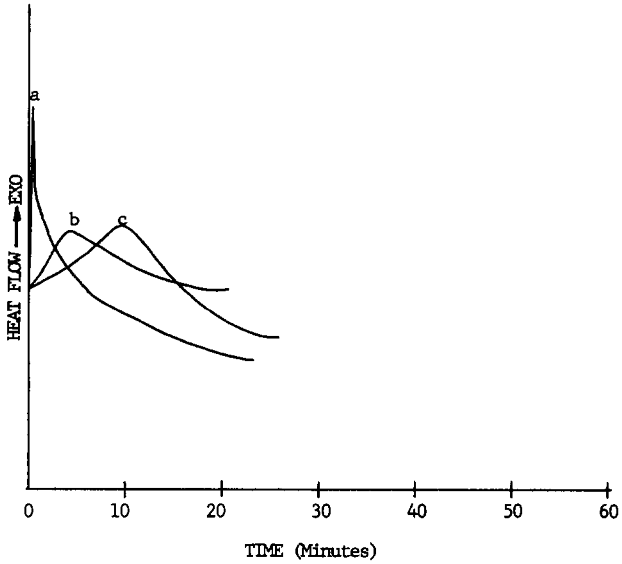


Fig. 3. HPDSC of purified resin acids at 550 psi $O_2$ and 130°C. (a) Abietic acid, (b) palustric acid, (c) isopimaric acid.

small peak. The sample of abietic acid was not as pure as the other samples, only 83.1% pure by ultraviolet spectrophotometry (UV). By contrast, a UV analysis of dehydroabietic acid showed > 99% purity.

TABLE 2

HPDSC of rosin products

| Sample | Temp. (°C) | HPDSC exotherm (min) | Exotherm calculated at 100°C (min)[a] |
|---|---|---|---|
| Hydrogenated rosin | 140 | 14 | 224 |
| More highly hydrogenated rosin | 140 | 18 | 290 |
| Polymerized rosin | 120 | 9.4 | 38 |
| Disproportionated rosin | 120 | 80 | 320 |
| | 130 | 38 | 304 |
| | 140 | 19 | 304 |
| | 150 | 8.8 | 282 |
| | 160 | 5 | 320 |
| Glycerine ester[b] | 130 | 13 | 104 |
| Pentaerythritol ester[b] | 130 | 16.5 | 132 |

[a] Assuming a two-fold change in rate for a 10°C change in temperature.
[b] Of more highly hydrogenated rosin.

## RESULTS AND DISCUSSION

### *Factors affecting oxidative stability*

One of the main factors determining the stability of a substance to a free radical oxidation is its molecular structure. The initial step is removal of an H atom followed by a rapid reaction of molecular oxygen with the free radical residue to form a peroxy radical

$RH \rightarrow R^{\cdot} + H^{\cdot}$

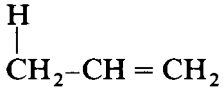
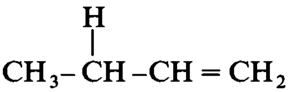
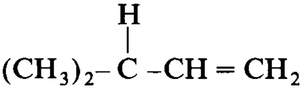
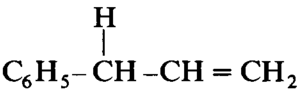
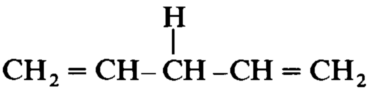
$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$

This initiation step can come about from thermally excited molecules, free radicals, metal catalysts or light. Chain propagation of the above reaction involves the removal of H by the peroxy radical in a slow reaction which determines the overall reaction rate.

$RO_2^{\cdot} + RH \rightarrow RO_2H + R^{\cdot}$

According to Walling [6], reaction rate will depend in part on the C–H bond strengths, which predict that tertiary H atoms are oxidized more readily than secondary H atoms, which are oxidized faster than primary H atoms. Allylic H atoms (–CH=CH–C–$\underline{H}$) are very susceptible to oxidation, presumably because the resulting radical is stabilized by resonance [7].

Bateman [8] and Bolland [9] have contributed much to this field by providing comparative rate data for free radical oxidations of various structures. A few of Bolland's examples are given below to illustrate the structure/activity relationship. The H atom under attack is singled out, and *k* represents relative reaction rates.

| Structure | *k* = reactivity |
|---|---|
|  $\overset{H}{CH_2}-CH=CH_2$ | 1 |
|  $CH_3-\overset{H}{CH}-CH=CH_2$ | 3.3 |
|  $(CH_3)_2-\overset{H}{C}-CH=CH_2$ | 10.9 |
|  $C_6H_5-\overset{H}{CH}-CH=CH_2$ | 23 |
|  $CH_2=CH-\overset{H}{CH}-CH=CH_2$ | 107 |

Although such data help us to understand, in part, the relationship of structure to reactivity, Bateman points out that other factors can complicate the picture. For example, one of the important termination steps in a free radical oxidation is the reaction of two peroxy radicals to form nonradical products.

$2\ RO_2^{\bullet} \rightarrow$ nonradical products

If the above reaction is fast, then the peroxy radicals are used up in a nonproductive (nonradical) route, and the overall oxidation rate is slower.

In addition to molecular structure, two other factors which can affect oxidation rate are the presence of a metal catalyst and the presence of an inhibitor. A metal catalyst can increase oxidation rate by increasing the rate of the initiation step. On the other hand, the presence of an inhibitor or antioxidant, whether natural or added, would decrease the overall oxidation rate by donating an H atom to the peroxy radical and forming a radical much more stable than the free radical which would have been formed in the absence of the stabilizer (R'OH = inhibitor).

$RO_2^{\bullet} + R'OH \rightarrow RO_2H + R'O^{\bullet}$ (more stable)

$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}$ (less stable radical)

## *Oxidizability of rosin products*

Most pale wood rosins which were analyzed by HPDSC exhibited exotherms in 10–13 min at 100°C. The exception was the sample of fines which exothermed in 6 min (see Fig. 1), showing that a sample which is partially oxidized (fines would have much more surface area for attack by $O_2$) will oxidize more readily than one which is not.

The greater oxidative stability of gum rosin than either wood rosin or TOR would suggest the presence of more natural inhibitor in gum rosin.

From Table 2 it can be seen that polymerization of rosin resulted in an increase in oxidative stability presumably because some of the abietic acid-type double bonds were reacted during polymerization.

Hydrogenation was even more effective in stabilizing rosin from oxidative attack, and a greater degree of hydrogenation resulted in greater oxidative stability.

Disproportionation of rosin was even more effective than hydrogenation in improving oxidative stability. On the other hand, esterification of hydrogenated rosin resulted in a decrease in oxidative stability which would suggest that bonds formed during the esterification were more prone to oxidation than the bonds in hydrogenated rosin.

TABLE 3

HPDSC of purified rosin acid structures

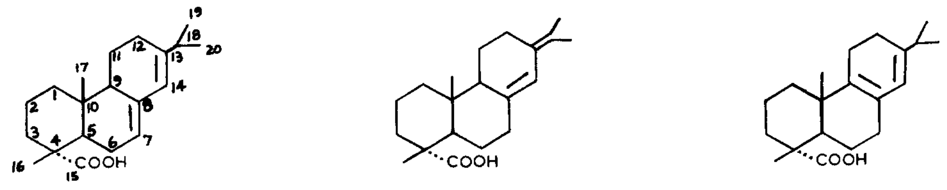
| Rosin acid | Temp. (°C) | HPDSC Exotherm (min) | Exotherm Calculated at 100°C (min) [a] |
|---|---|---|---|
| Dehydroabietic acid | 160 | 24 | 1536 |
| Abietic acid | 130 | <1 | 1 |
| Neoabietic acid | 130 | <1 | 1 |
| Levopimaric acid | 130 | <1 | 1 |
| Isopimaric acid | 130 | 10 | 80 |
| Palustric acid | 130 | 4 | 32 |

[a] Assuming a two-fold change in rate for a 10°C change in temperature.

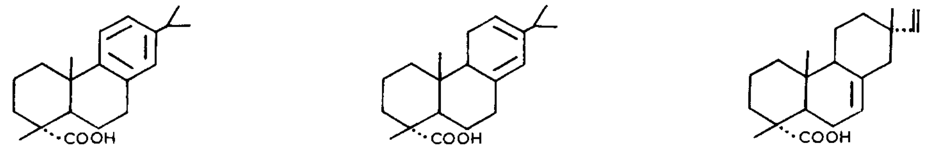
### *Oxidizability of purified resin acids*

By examining the HPDSC results in Table 3, it is obvious that dehydroabietic acid is the most stable by far of the six structures studied. At 160°C the oxidation exotherm time was 24 min. Assuming a two-fold change in rate for each 10°C change in temperature, the estimated time at 100°C would have been $2^6 \times 24$ or 1536 min. Considering that pale wood rosin exotherms in about 11 min at 100°C, dehydroabietic acid is more stable to oxidation than wood rosin by a factor of $> 10^2$.

By observing the rosin acid structures in Fig. 4, it is not surprising to find that isopimaric acid is the next most stable structure after dehydroabietic



ABIETIC ACID NEOABIETIC ACID PALUSTRIC ACID



DEHYDROABIETIC ACID LEVOPIMARIC ACID ISOPIMARIC ACID

Fig. 4. Resin acid structures.

acid. With a calculated exotherm time of 80 min at 100°C, isopimaric acid is about 20 times less stable to oxidation than is dehydroabietic acid. It is much more stable to oxidation than the other rosin acids containing two double bonds. The quaternary carbon atom at position 13 in isopimaric acid prevents the exocyclic double-bond from being part of a conjugated system.

Of the four remaining structures in Table 3, we were not able to differentiate between abietic acid, neoabietic acid and levopimaric acid. They all exothermed almost immediately at 130°C giving an estimated exotherm time of about 1 min at 100°C, indicating that dehydroabietic acid was about 1500 times more stable to oxidation than these three abietic acid-type structures.

Palustric acid, even though it possesses two conjugated double bonds, showed a 4-min exotherm at 130°C which translates to 32 min at 100°C. It is still much less stable (by a factor of ca. 50) than dehydroabietic acid. This greater stability suggests that the 8 to 9 double bond common to both rings is not as effective in activating an allylic H atom as a double bond which is not common to two rings.

## CONCLUSION

HPDSC was used successfully to determine the oxidative stability of various rosins and rosin products. In general results were consistent with established principles of free radical chemistry which relate structure and susceptibility to oxidation.

## ACKNOWLEDGMENTS

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## REFERENCES

1 H.F. Mark and A. Standen (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, 2nd edn., Wiley, New York, 1968, Vol. 17, p. 491.

2 F. Noel, J. Inst. Pet., 57 (1971) 357.

3 J.A. Walker and W. Tsang, Soc. Auto Eng., 801383 (1980) 1.

4 M. Yamazaki. A. Nagao and K. Komamiya, J. Am. Oil Chem. Soc., (1980) 59.

5 G. Dugan and J.D. McCarty, Proc. 13th North American Thermal Analysis Soc., Philadelphia, PA, 1984, p. 520.

6 C. Walling, Free Radicals in Solution, Wiley, New York, 1957, p. 417.

7 R. Stewart, Oxidation Mechanisms, Benjamin, New York, 1964, p. 14.

8 L. Bateman, Q. Rev. Chem. Soc., 8 (1954) 147.

9 J.L. Bolland, Trans. Faraday Soc., 46 (1950) 358.