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Thermal Reactivity of Poly(styrene peroxide): A Thermodynamic Approach

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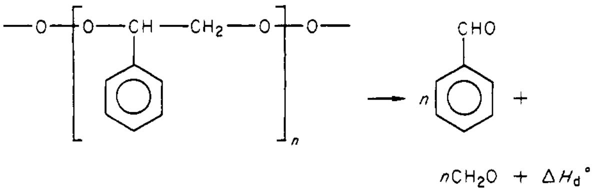
Polymeric peroxides are an important class of compounds and in the past a significant amount of work has been reported by Mayo et al.[1-3] and Cais.[4] The literature on polymeric peroxides has also been reviewed recently.[5] Poly(styrene peroxide) (PSP) decomposes exothermically; however, no justification for the exothermic nature of the reaction is available. This note attempts to explain the exothermicity of PSP decomposition by thermodynamic considerations.

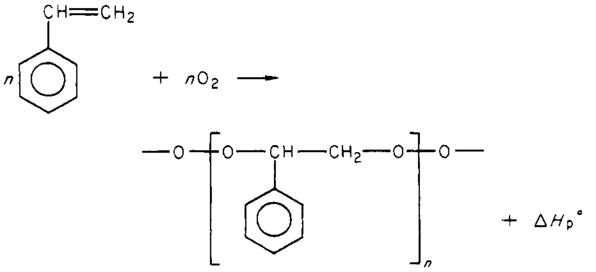
It is known that PSP decomposes to give benzaldehyde and formaldehyde as major products, with the evolution of heat.[2,6] Recent studies from this laboratory using pyrolysis gas chromatography have confirmed that formaldehyde and benzaldehyde are the major products of degradation (95-97%) in the temperature range 120-350 °C.[7] The degradation can be expressed as



(1)

In order to calculate the heat of degradation ($\Delta H_d°$), one must known the heat of formation ($\Delta H_f°$) of PSP. This was evaluated from (i) the heat of polymerization ($\Delta H_p°$) and (ii) the heat of combustion ($\Delta H_c°$).

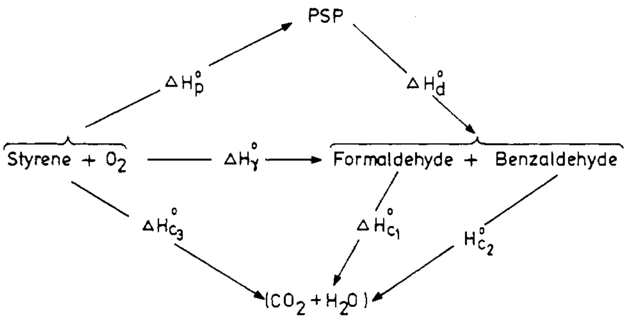
(i) PSP is formed by the reaction of O_2 with styrene:



(2)

In this process a C=C and an O=O bond are broken to form one O-O, one C-C, and two C-O bonds. Using Table II, one calculates the value of $\Delta H_p°$ for PSP to be 20.9 kcal mol^{-1}. However, $\Delta H_p°$ is also dependent upon structural factors. For example, in vinyl polymerization the breakage of one C=C bond gives rise to two C-C bonds and the heat evolved in the process is 19.8 kcal mol^{-1}, as compared to 16.8 kcal mol^{-1} for the experimental value of $\Delta H_p°$ for polystyrene (Table I). Taking into consideration the structural factors, we therefore take the actual $\Delta H_p°$ value for PSP to be 18 kcal mol^{-1}. Using this value and the $\Delta H_f°$ for styrene, we calculate the $\Delta H_f°$ for PSP to be 7 kcal mol^{-1} and that for PS to be 8 kcal mol^{-1}.

Scheme I



(ii) $\Delta H_c°$ of PSP was experimentally measured with a Parr 1243 automatic adiabatic bomb calorimeter attached to a 1680 master control. Correction for the formation of HNO_3 and the heat of combustion of the fuse wire and cotton was made. The instrument was calibrated with standard benzoic acid pellets supplied by Parr. The experimental value of $\Delta H_c°$ for PSP was found to be 1032 ± 5 kcal mol^{-1}. Utilizing these data and the $\Delta H_f°$'s for CO_2 and H_2O, we calculate the $\Delta H_f°$ for PSP to be 6 kcal mol^{-1}.

A mean value of 6.5 kcal mol^{-1} was presumed to be the heat of formation of PSP on the basis of the $\Delta H_f°$ for PSP obtained from the data of heat of polymerization and the heat of combustion (7 and 6 kcal mol^{-1}, respectively). The $\Delta H_f°$ evaluated independently from the heat of polymerization and $\Delta H_c°$ are similar, showing consistency in the derived $\Delta H_f°$ value.

$\Delta H_d°$ for PSP was calculated by four different procedures.

(1) Using $\Delta H_f°$, we calculated theoretically from eq 1 the heat change during PSP decomposition.

$$\Delta H_f°(\mathrm{PSP}) \rightarrow \Delta H_f°(\mathrm{C_6H_5CHO}) + \Delta H_f°(\mathrm{CH_2O}) + \Delta H_d° \quad (3)$$

It was found to be -52 kcal mol^{-1}.

(2) $\Delta H_d°$ was calculated from bond dissociation energies. During the process of PSP degradation (eq 1) one C-C bond and one C-O bond are broken while two C-O bonds are converted to two C=O bonds, and formaldehyde is vaporized. The calculated enthalpy change ($\Delta H_d°$) for this process is -50.3 kcal mol^{-1}.

(3) Scheme I together with Hess' law was used. $\Delta H_{c_3}°$, the heat of combustion of styrene (-1050 kcal mol^{-1}), was obtained from the following equation, employing $\Delta H_f°$ from Table I:

$$\mathrm{C_8H_8(l)} + 10\mathrm{O_2} \rightarrow 8\mathrm{CO_2} + 4\mathrm{H_2O} + \Delta H_{c_3}° \quad (4)$$

Since

$$\Delta H_c°(\text{styrene}) \rightarrow \Delta H_c°(\text{PS}) - \Delta H_p°(\text{styrene}\rightarrow\text{PS}) \quad (5)$$

and $\Delta H_c°$ and $\Delta H_p°$ for PS are known (Table I), $\Delta H_c°$ of styrene was again obtained as 1052 kcal mol^{-1}. The reported value of $\Delta H_c°$ for styrene (1019 kcal mol^{-1}) in ref 8 thus seems to be incorrect. $\Delta H_r°$ as represented in Scheme I was obtained from $\Delta H_f°$ data (Table I) as 70.3 kcal mol^{-1}. Using Tables I and II, we also calculated independently $\Delta H_r° = 71.6$ kcal mol^{-1}. $\Delta H_f°$ was thus taken

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Table I
Thermochemical Data[a]

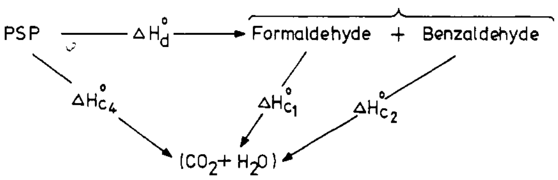
compound	$\Delta H_f°$, kcal mol^{-1} value	ref	$\Delta H_c°$, kcal mol^{-1} value	ref	$\Delta H_v°$,[b] kcal mol value	ref
styrene(l)	24.83	11	1019 1051	8 this work	10.6	8
polystyrene	8.0	this work	1035	9		
benzaldehyde(l)	−17.8	11	843.2	10, 12	11.6	10
formaldehyde(g)	−27.7	10, 11	136.42	8, 12	5.92	10
carbon dioxide(g)	−94.05	10, 11				
water(l)	−68.32	12				
poly(styrene peroxide)	6.5	this work	1032	this work		

[a] $\Delta H_p°$ for PS from styrene = 16.8 kcal mol^{-1}. $\Delta H_p°$ for PSP as calculated from bond energy = 18.0 kcal mol^{-1} (this work) work). [b] Heat of vaporization.

Table II
Bond Energy Data

bond type	bond energy, kcal mol^{-1}	ref
C=C	145.8	12-14
C=C	82.8	12-14
C=O		
formaldehyde	166	14
other aldehydes	176	12-14
C—O	85.5	12-14
O—O	119.1	14
O—O	32	12

Scheme II



as 71 kcal mol^{-1}. $\Delta H_{c_1}°$ and $\Delta H_{c_2}°$ are the heats of combustion of aldehydes (Table I). $\Delta H_{c_3}°$ was thus calculated to be 1050 kcal mol^{-1} using eq 6, which gives excellent

$$\Delta H_{c_3}° = \Delta H_r° + \Delta H_{c_1}° + \Delta H_{c_2}° \qquad (6)$$

agreement with $\Delta H_c°$ for styrene. $\Delta H_r°$ = 71 kcal mol^{-1} should also be equal to the sum of $\Delta H_p°$ and $\Delta H_d°$ of PSP. Since $\Delta H_p°$ of PSP is known (Table I), $\Delta H_d°$ was calculated to be −53 kcal mol^{-1}.

(4) The cycle in Scheme II permits the following equation to be written:

$$\Delta H_d° = \Delta H_{c_4}° - \Delta H_{c_1}° - \Delta H_{c_2}° \qquad (7)$$

Using the data from Table I, we find $\Delta H_d°$ to be −52.4 kcal mol^{-1}. Based on the values from the four methods (−52.0, −50.3, −53.0, and −52.4 kcal mol^{-1}), a mean value of −52 kcal mol^{-1} could be assigned for $\Delta H_d°$ for PSP. The calculated value of $\Delta H_d°$ for PSP suggests that the process should be exothermic in nature.

Experimentally, $\Delta H_d°$ was measured with a Du Pont differential scanning calorimeter. No residue was found in the pan. A typical DSC thermogram is shown in Figure 1. The enthalpy was calculated from the area under the peak in the usual manner. Correction was made for the volatilization of the degradation products benzaldehyde and formaldehyde by using the data from Table I. The resulting $\Delta H_d°$ for PSP was 50 ± 1 kcal mol^{-1}, which is comparable with the theoretically predicted $\Delta H_d°$ from $\Delta H_f°$ and bond dissociation energies. The small difference may arise from (i) the approximation involved in the input thermochemical data, (ii) lower yields of the aldehydes under the experimental conditions, and (iii) occurrence of minor side reactions during PSP degradation. Pyrolysis gas chromatographic results have shown the formation of some minor products in addition to benzaldehyde and formaldehyde.[7]

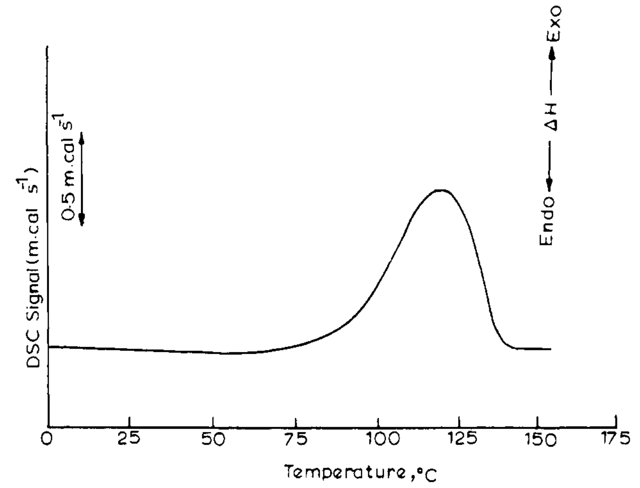


Figure 1. DSC thermogram of PSP.

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