Physicochemical behaviour of polyperoxides

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Polymeric peroxides are equimolar alternating copolymers formed by the reaction of vinyl monomers with oxygen. Physicochemical studies on the microstructure and chain dynamics of poly(styrene peroxide) PSP were first carried out by Cais and Bovey. We have found that polyperoxides are formed as main intermediates in solid-propellant combustion by the interaction of the monomer and oxygen generated by the decomposition of the polymeric binder and the oxidizer ammonium perchlorate. The experimentally determined heat of degradation and that calculated from thermochemical considerations reveal that polyperoxides undergo highly exothermic primary degradation, the rate-controlling step being the O–O bond dissociation. A random-chain scission mechanism for the thermal degradation of polyperoxides has been proposed. The prediction of unusual exothermic degradation of polyperoxides has resulted in the discovery of an interesting new phenomenon of 'auto-pyrolysability' in polymers. Several new polyperoxides based on vinyl naphthalene have been synthesized. We have also found that PSP, in conjunction with amines, can be used as initiator at ambient temperature for the radical polymerization of vinyl monomers.

In the fascinating world of polymers, small alterations in structure at the molecular level induce large changes in macroscopic properties. For example, the contrasting behaviour of thermally stable flame-retardant polymers and thermally unstable combustible polymers arise out of the sensitivity of their backbone, towards heat. This account deals particularly with studies of the latter category of polymers wherein weak links, such as peroxides, have been introduced intentionally into the backbone by reacting vinyl monomers with oxygen. Unintentionally, molecular oxygen could also introduce weak peroxy linkages into the main chain of vinyl polymers during commercial polymerization.

The effect of an oxygen atmosphere in both retarding (resulting in an induction period) and enhancing the post-induction period rate, of free radically initiated vinyl polymerization is a paradox[1]. This impasse was overcome, with an increased understanding of the polymeric peroxides which are macromolecular counterparts of simple organic peroxides like di-*t*-butyl peroxide. The peroxides, in general, are formed (Figure 1) by the (i) addition of H_2O_2, alkyl hydroperoxides or percarboxylic acids to the carbonyl group of aldehydes or ketones (I); (ii) auto-oxidation of alcohols, ethers, aldehydes, alkanes, alkenes, etc. (II); and (iii) ozonization of unsaturated compounds (III). The polymers in question, under the present review, are alternating copolymers of vinyl monomers (Figure 1, IIc) and oxygen which have been the focus of attention in the authors' laboratory.

The retardation in vinyl polymerization in an oxygen atmosphere was attributed to the formation of a polymeric peroxide at the top layer of the monomer in contact with oxygen and the enhancement in the post-induction rate, to the extra radicals generated by the decomposition of unstable polyperoxides[1]. Since the first report on the formation of a polymeric peroxide by Staudinger in 1922, the bulk of the literature on polyperoxides dwells upon their mechanism and kinetics of formation and degradation, and the effects of oxygen pressure on these[2]. About eighteen polyperoxides were reported during this period[2], but poly(styrene peroxide) (PSP) was the one chosen by most authors for

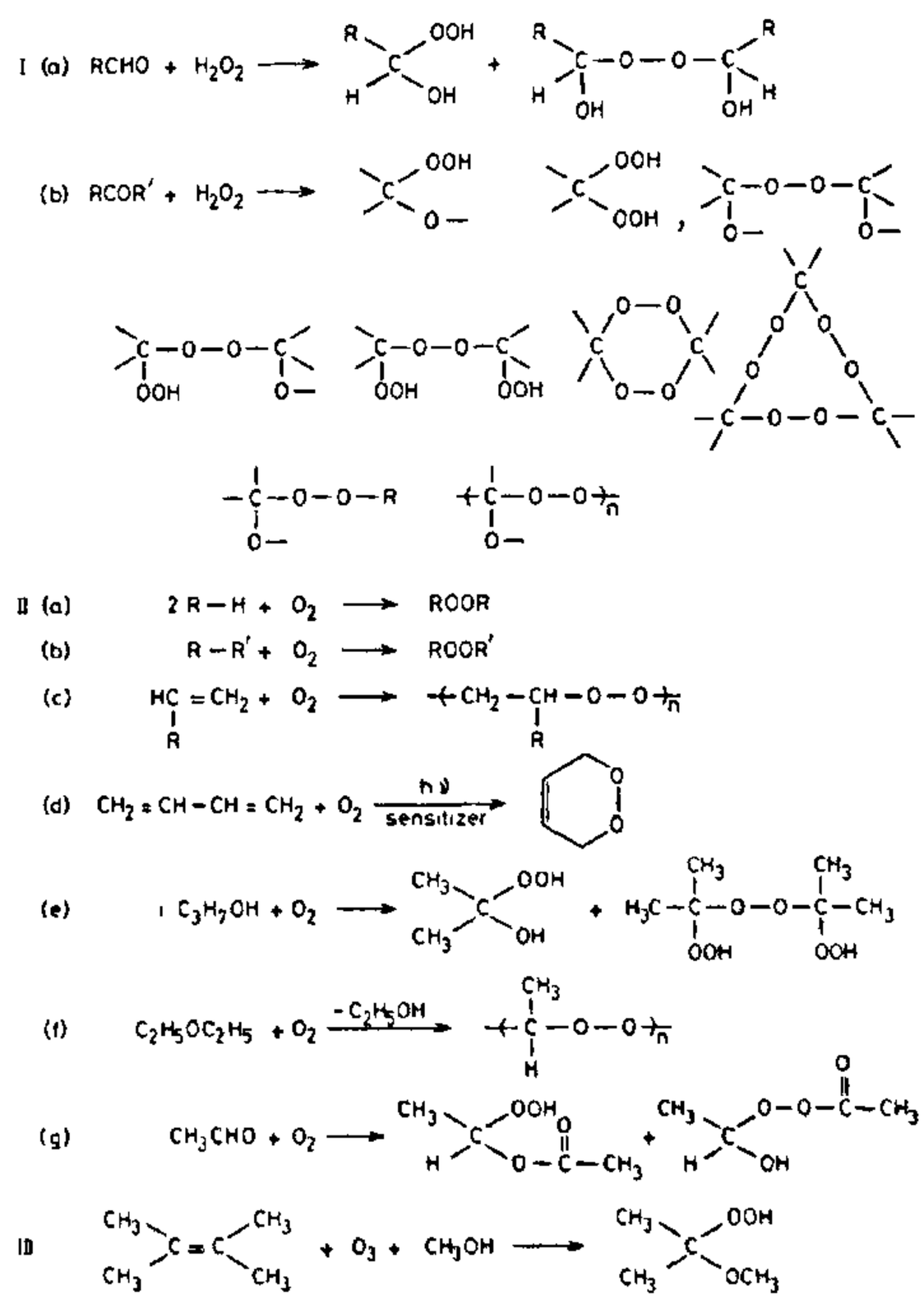


Figure 1. Formation of peroxides

detailed studies. These thorough studies on PSP and other polyperoxides, stimulated by the paradoxical effect of oxygen on vinyl polymerization, however, led to the emergence of a new class of polymers, viz. the polymeric peroxides—the equimolar, alternate copolymers of vinyl monomers and oxygen. Surprisingly, none of the reports in this period discussed the physical or chemical properties of this class of polymers.

The first attempt at characterizing this new class of polymers was by Cais and Bovey[3] in 1977, when they discussed the microstructure and chain dynamics of PSP. A preliminary report[4] on optically active PSP also appeared around the same time. Polyperoxides were observed as key intermediate in combustion, in this laboratory[5]. They were also used as natural catalysts for burning rate modification in solid propellants. Thermal degradation of many polyperoxides was studied in this laboratory. Subsequently, the application of the thermodynamic calculations[6,7] on their degradation and the quantification of the heats of degradation[6,7] of these polyperoxides resulted in the detection of the recently reported auto-pyrolysis and auto-combustion in PSP[9]. The most recent studies on the physicochemical properties of polyperoxides involve the base[10] and light-assisted initiator capabilities of PSP for room temperature radical polymerization. These developments, which have taken place in the past decade, are the subject of this account. Beginning with the microstructure and chain dynamics of PSP, we discuss the key intermediacy of polyperoxides in combustion, thermal reactivity and energetics of degradation of polyperoxides, the role of polyperoxides as initiators and the novel phenomenon of auto-pyrolysis and its application in developing a novel fuel based on polyperoxides.

Microstructure of poly(styrene peroxide)

In a classic paper in 1977 Cais and Bovey[3] described, a detailed ^{13}C NMR study of the microstructure and molecular dynamics of PSP. This was the first report on the study of the physical or chemical properties of polymeric peroxides. The ^{13}C NMR spectrum of PSP is shown in Figure 2. An expanded version of the phenyl carbon resonances of the polyperoxide shows the *ortho* carbons at higher field than the *meta* and *para*. These assignments have been made based on the chemical shifts in the model compound α-methylbenzyl alcohol. However, this is contrasted with the polystyrene spectrum, in which the *para* carbon appears at higher field than the *ortho* and *meta* carbons. Furthermore, these assignments (of the *ortho* and *meta*, *para* carbons) in PSP also contrast the ^{1}H NMR spectrum of polystyrene. It may be noted that the 60 MHz ^{1}H NMR spectrum of PSP shows a singlet, unlike in PS where *ortho* (upfield) and *meta*, *para* (downfield) are well

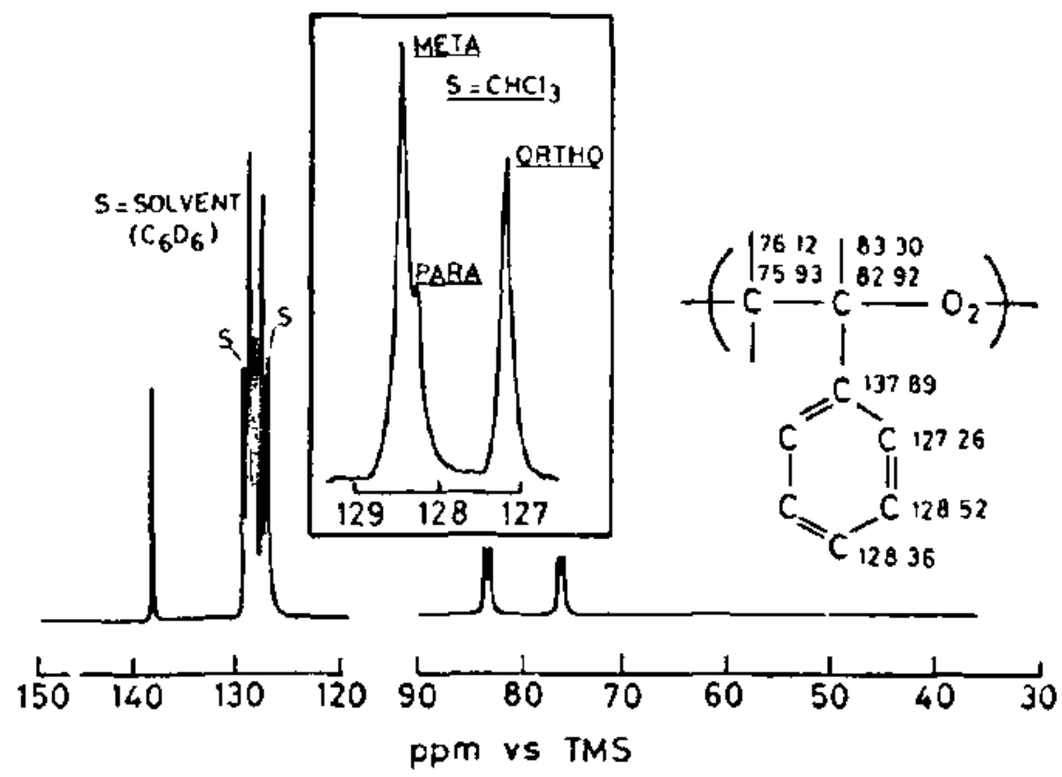


Figure 2. ^{13}C NMR spectrum of PSP (25 16 MHz) (from ref. 3, with permission).

resolved. The 360 MHz ^{1}H NMR spectrum of PSP (Figure 3) shows the *ortho* downfield than *meta*, *para*. This is rather expected, as in PSP with the phenyl rings with the peroxo group spacers in between are further apart, than they are in PS and hence do not hinder the rotation of the phenyl ring along the C–α and C– ipso bond. The *ortho* protons thus experiencing magnetic equivalence, in the vicinity of the O atom of the peroxide, get deshielded and show a downfield chemical shift.

It can be seen from the ^{13}C spectrum that, only the main-chain α and β carbons in the polyperoxide exhibit resolved fine structure. They give doublets of equal intensity (resolved almost to the base line at 90.52 MHz[3]) indicating that there are two magnetically non-equivalent environments for these nuclei. These must reflect configurational dyad placements of equal probability. It has also been shown that the backbone carbons show identical configurational sensitivity and that the aromatic carbons are insensitive. This is in

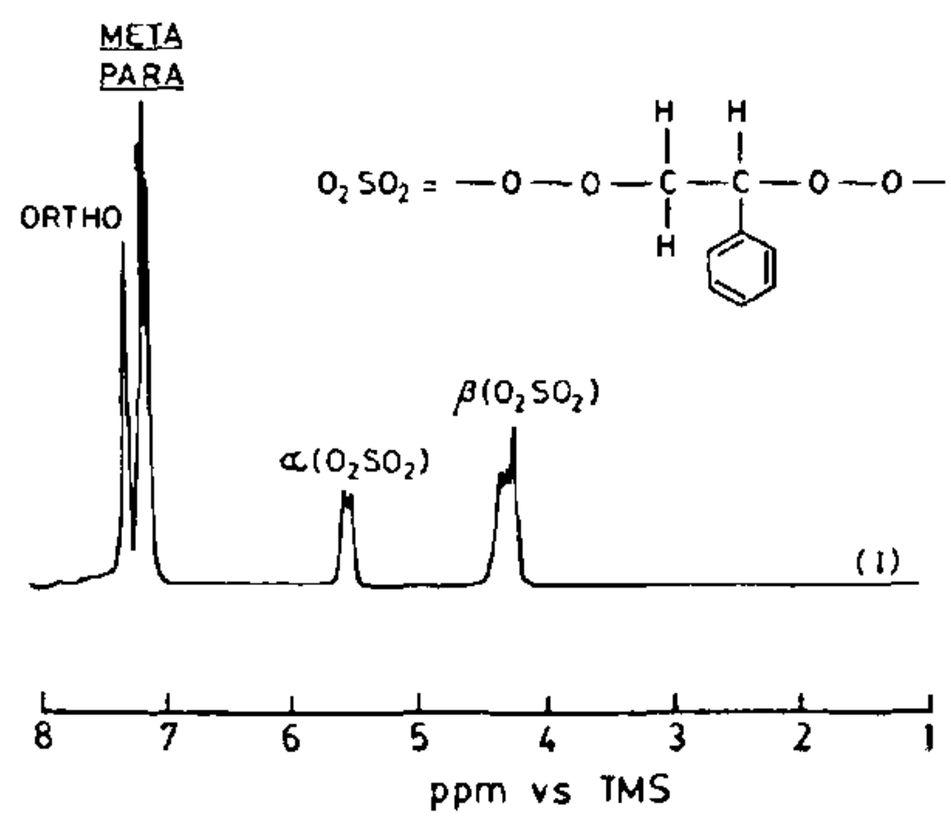


Figure 3. ^{1}H NMR spectrum of PSP (360 MHz) (from ref. 3, with permission).

contrast to what is observed for polystyrene, where only the quaternary and β-carbons show configurational splitting.

The equal probability of m and r dyad placements indicates that the configurational propagation statistics for the equimolar polyperoxide follow the 'ideal' Bernoullian case, i.e. $p(m) = p(r) = 0.5$, where $p(m)$ and $p(r)$ are the unconditional probabilities for the formation of meso and recemic dyads respectively. In general, in free radical vinyl homopolymerization there is observed a biased Bernoullion statistics, with $p(r) > P(m)$. In PSP, the increased spacing of the asymmetric centres, introduced by the peroxide unit removes any such bias, which is normally steric in origin.

Chain dynamics of poly(styrene peroxide)

Cais and Bovey using ^{13}C relaxation time measurements and nuclear Overhauser enhancement measurements have studied the chain dynamics of PSP. Using T_1 values for resolvable carbons of PSP and comparing with those for atactic polystyrene of low-molecular weight, they have drawn conclusions on the flexibility of PSP chains. The 2:1 ratio of T_1 values for α- and β-carbons confirmed the dipole–dipole nature of the backbone carbons relaxation ($\alpha = 0.24$, $\beta = 0.12$ at 33°C in $CHCl_3$ at concentration of 22 wt%). The data show that the polyperoxide is substantially more flexible than polystyrene, the main chain T_1 values being longer by a factor of 2, under comparable conditions ($\alpha = 0.10$, $\beta = 1055$ at 33°C in $CHCl_3$ at concentration of 22 wt%) but is less flexible than poly(methyl oxirane) of comparable molecular weight, for which the C_α carbons have T_1 values nearly four-fold larger.

For polystyrene, the relaxation of the phenyl C_2 and C_3 carbons is comparable to that of the C_α and C_4 carbons (the latter two being necessarily at least approximately equal since they share the same motion), indicating limited rotational motion. In the polyperoxide, by contrast, the C_2 and C_3 relaxation times are 1.6 times those of C_α and C_4, showing that they enjoy a considerable measure of additional rotational freedom, a peroxide oxygen atom being less sterically restrictive than a β-methylene group.

An estimate of the phenyl group rotational time in relation to chain segmental motion and overall tumbling may be made using the approximate relationship.

$$\frac{1}{T_c(\Phi, \text{obs})} = \frac{1}{T_c(\Sigma)} + \frac{1}{T_c(\Phi)}$$

here $T_c(\Phi, \text{obs})$ is the correlation time for the phenyl group calculated from T_1 of the C_2, C_3 carbons. $T_c(\Sigma)$ is the correlation time for overall chain motion similarly calculated from the T_1 values for C_α and C_β and $T_c(\Phi)$ is the correlation time of the phenyl group, apart from the contribution of the main chain. From the values of $T_c(\Sigma)$ and $T_c(\Phi)$ at different temperatures, approximate values of the activation energies for overall tumbling-plus-segmental motion and for phenyl group rotation have been calculated—20 and 27 kJ mol^{-1} respectively. For poly(methyl oxirane) of low-molecular weight, in chloroform, the reported values for overall tumbling-plus-segmental motion and methyl group rotation are 21 and 11 kJ mol^{-1} respectively.

By assuming a gauche conformation and the C_1–H distances described in the microstructure of PSP given in Figure 4, an approximate calculation of the T_1 of the quaternary carbon C_1 has been carried out. It is found that, allowing for the contributions from neighbouring chain units, the calculated and observed values of T_1 at 33 and 45°C are in good agreement.

These ^{13}C studies have revealed the microstructure and the chain flexibility of PSP. This has also paved way for similar interesting studies of the general class $(-CH_2-CHR-X-)$[11–13], where X is a heteroatom or a group of heteroatoms.

The intermediacy of polymeric peroxides in combustion reactions

The occurrence and the significance of condensed phase reactions in composite solid propellants have been studied[14]. The propellants examined typically comprised an organic hydrocarbon polymer as fuel-binder and ammonium perchlorate (AP) as oxidizer. Amongst the several organic combustion intermediates analysed from the quenched combustion residues of a model propellant based on polystyrene (PS) and AP or PS and potassium perchlorate (KP), the existence of a polymeric intermediate containing in-chain peroxy linkage was deduced from chemical analysis[5]. The most probable in-chain peroxide formed could be the PSP. The detected benzoic acid[15] could have resulted only from the degradation of PSP fragment that must have formed as the said in-chain peroxy intermediate. Under the conditions of propellant combustion the binder polymer (PS) depolymerizes and gives out styrene

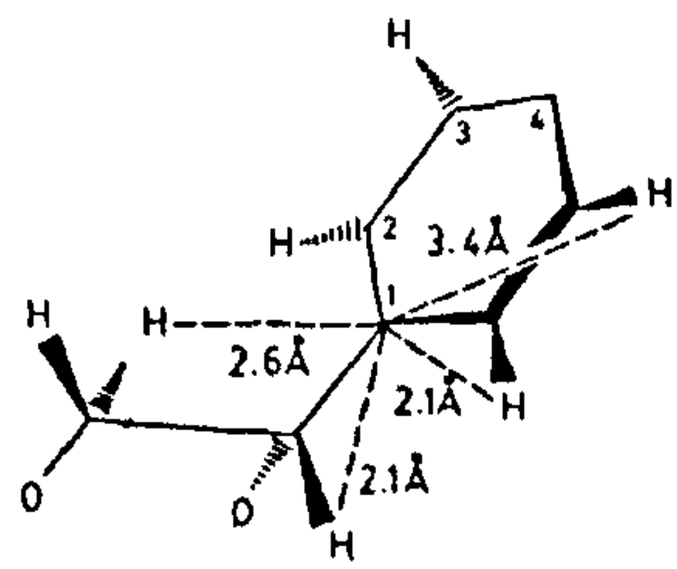


Figure 4. Gauche conformation of PSP (from ref. 3, with permission).

monomer, which *in situ* interacts with oxygen from AP, KP, to form PSP.

Degradation kinetics of polyperoxides

The thermal degradation of PSP was studied using DSC by adopting multiple heating rates method for evaluating kinetic parameters[16]. The following equation was used for the purpose.

$$\frac{S}{\Delta H} = (1-\alpha)^n A \exp(-E/RT),$$

where S is the ordinate deflection in mcal s^{-1}; ΔH the heat of degradation of PSP; A the frequency factor, and R the gas constant. Activation energy E was obtained by plotting $\ln S/\Delta H$ vs $1/T$. For this plot, α and n were assumed constant, which were verified separately. Constancy of n was checked from reduced time plots by superimposing the fraction decomposed vs time (t) plot (Figure 5) at various heating rates. Constancy of α was assured by carrying out the E value evaluation at a particular value for all the dynamic curves. The E value in the entire range of decomposition was consistent, and found to be 136 ± 9 kJ mol^{-1}, which agreed well with O–O bond dissociation energy. This result was also in agreement with isothermal thermogravimetry (TG) studies, which gave an E value of 30 kcal mol^{-1} (the temperature range studied here is 75–105°C; the high-temperature decompositions were too fast to be followed). The activation energies for polyperoxide degradation were also obtained in other polyperoxide samples as well, using another multiple heating rate method, viz. the Kissinger's method[17,18]. The values obtained were consistent with the O–O bond dissociation energy (37 ± 2 kcal mol^{-1}).

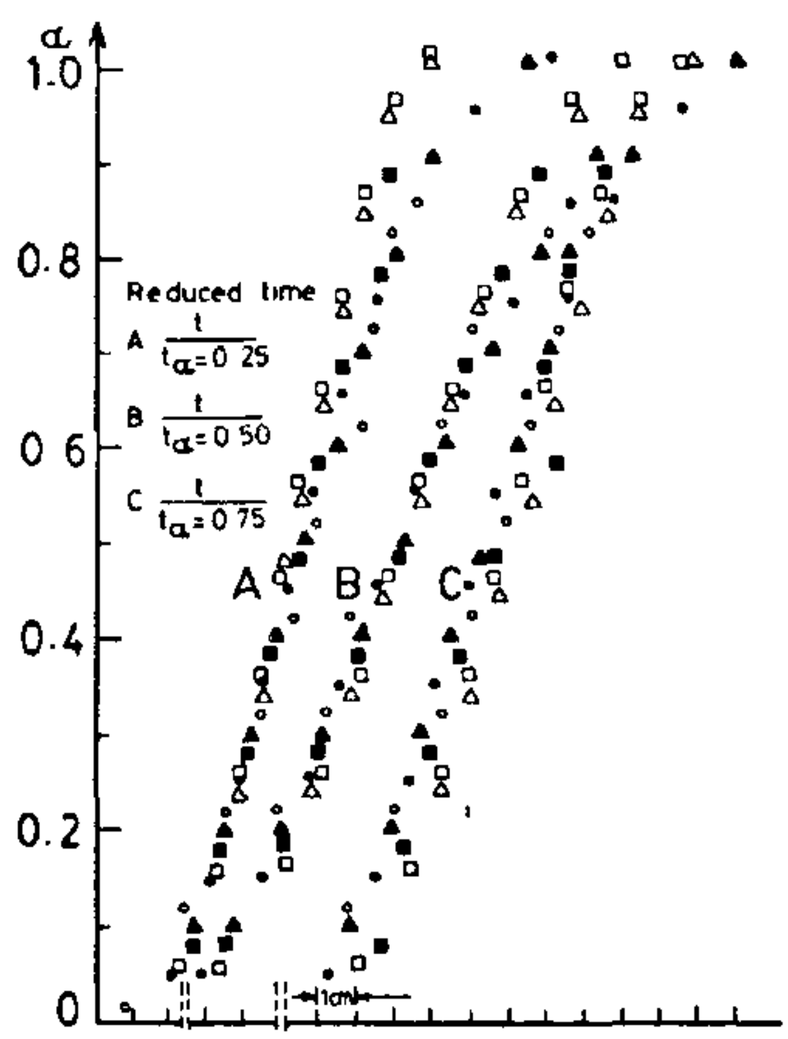


Figure 5. Fraction degraded vs reduced time plots at various stages of degradation, Heating rate (C min^{-1}). ○2; △4, □8; ■16, ▲32, ●64 (from ref. 16).

Table 1. Comparative study of the thermal degradation of various polyperoxides of the present study* (taken from ref. 2).

Polyperoxide	DSC peak temperature (°C)	Actual heat of degradation (kJ mol^{-1})
PSP	149.1 ± 1.0	−209 ± 8
PMMAP	145.4 ± 1.0	−184 ± 8
PVNP2	112.9 ± 1.0	−206 ± 4
PMVNP1	135.4 ± 1.0	−222 ± 8
PMVNP2	135.2 ± 1.0	−222 ± 10
PDVBP**	147.5 ± 1.5	—

*A heating rate of 10 C min^{-1} has been maintained in all the cases.
**Poly(1,4-divinylbenzene peroxide). The polymer in this case was a cross-linking one, therefore, the exact structure and hence the ΔH_d^0 could not be determined.

Thermochemistry of degradation of polyperoxides

Heats of degradation

The heat of degradation of various polyperoxides, namely PSP; poly(methyl methacrylate peroxide) (PMMAP); poly(2-vinylnaphthalene peroxide), (PVNP2); poly(1,α-methylvinylnaphthalene peroxide), (PMVNP1), and poly(2,α-methylvinylnaphthalene peroxide), (PMVNP2), were measured from differential scanning calorimetry at different heating rates[2,6–8]. The product of degradation, namely formaldehyde and corresponding aldehydes or ketones account for more than 95% of the total degradation products in these polyperoxides. Since these products volatilize off from the pan, correction for the heat of vaporization of these species was incorporated in the calculation of the heat of degradation of (ΔH_d^0). The ΔH_d^0's of all the above mentioned polyperoxides are summerized in Table 1.

Thermochemical calculations on ΔH_d^0

The typical degradation of a polyperoxide can be represented as follows:

$$\text{Polyperoxide} \longrightarrow \text{aldehyde or ketone} + CH_2O + \Delta H_d^0 \quad (1)$$

Calculation of ΔH_d^0 for PSP and PMMAP is discussed below.

For calculating ΔH_d^0, one must know the ΔH_f^0 of PSP. This was obtained from the ΔH_p^0 and ΔH_c^0 data. For PSP (ref. 7), the polymerization reaction can be represented as,

$$\text{Styrene} + O_2 \longrightarrow \text{polyperoxide} + \Delta H_p^0 \quad (2)$$

In the polymerization process, one C=C and one O=O bonds are transformed into one C–C and two C–O single bonds. From bond energy values ΔH_p^0 was

found to be 20.9 kcal mol^{-1}. Since ΔH_p^0 also depends upon structural factors, corrections were applied on the basis of the difference in calculated ΔH_p^0 value (19.8 kcal mol^{-1}) of polystyrene calculated from bond-energy data and that obtained experimentally (16.8 kcal mol^{-1}). Considering the similarity in the structural features of PS and PSP, ΔH_p^0 of PSP was assigned as 18 kcal mol^{-1}. Substituting the ΔH_p^0 and ΔH_f^0 of styrene, ΔH_f^0 for PSP was found to be 7 kcal mol^{-1}. Similar calculations give ΔH_p^0 for PMMAP as 15 kcal mol^{-1} and ΔH_f^0 for PMMAP as -100.4 kcal mol^{-1}.

ΔH_f^0 for PSP was also obtained from experimentally measured ΔH_c^0 and was found to be 6 kcal mol^{-1}. Similarly, for PMMAP the ΔH_f^0 value is -114.7 kcal mol^{-1} (ref. 7). Average value of ΔH_f^0 obtained from ΔH_p^0 and ΔH_c^0 was thus assigned, for PSP and PMMAP, it is 6.5 kcal mol^{-1} and -107.6 kcal mol^{-1} respectively. ΔH_f^0, ΔH_p^0, ΔH_v^0 and ΔH_c^0 are given in Table 2. From the ΔH_f^0 of the products, PSP and PMMAP, the ΔH_d^0 for PSP and PMMAP was calculated using equation (1). The values were 52 kcal mol^{-1} and 42.2 kcal mol^{-1} for PSP and PMMAP respectively.

During degradation of these polyperoxides, one C–C and one O–O bonds are broken and two C–O bonds are transformed into two C=O bonds. This gives a value of ΔH_d^0 equal to -50.3 kcal mol^{-1} and -41.2 kcal mol^{-1}, for PSP and PMMAP respectively.

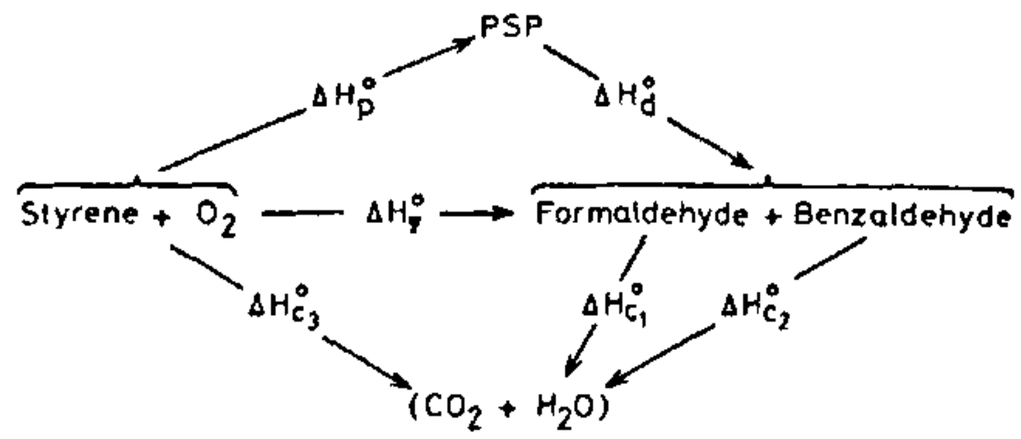
From the Hess's cycle (Scheme 1), ΔH_r^0 (the heat of the reaction for a hypothetical reaction) is obtained from ΔH_f^0 data. ΔH_c^0 of aldehydes and ketones are given Table 2. ΔH_r^0 was obtained from the ΔH_f^0's of C_6H_5 CHO, CH_2O and styrene. This could also be obtained from ΔH_c^0's. ΔH_r^0 from both these calculations were consistent. From Scheme 1, ΔH_d^0 could be obtained from ΔH_p^0 and ΔH_r^0. It was found to be -53 kcal mol^{-1} for PSP and -42.2 kcal mol^{-1} for PMMAP. Scheme 2 also gives ΔH_d^0 of -52.4 kcal mol^{-1} for PSP. The average value of ΔH_d^0 from the above calculations were -52 ± 2 kcal mol^{-1} and -44 ± 2 kcal mol^{-1} for PSP and PMMAP respectively.

The minor difference between the calculated and experimentally observed ΔH_d^0 could arise from the approximations in the input thermochemical data and the minor occurrence of side reactions such as disproportionation. These calculations show that polyperoxides degrade highly exothermically unlike the other polymers which degrade endothermically.

Table 2. Thermochemical data*.

Compound	ΔH_f^0	ΔH_p^0	ΔH_v^0	ΔH_c^0
Styrene	24.8	—	10.6	1051
PSP	6.5	18.0	—	1032
Φ CHO	−17.8	—	11.6	843.2
CH_2O	−27.7	—	5.9	136.4
Water	−68.3	—	—	—
MMA	−85.4**	—	—	—
Methyl pyruvate	−134.6**	—	12.6**	—
PMMAP	−107.6	—	—	626.6**

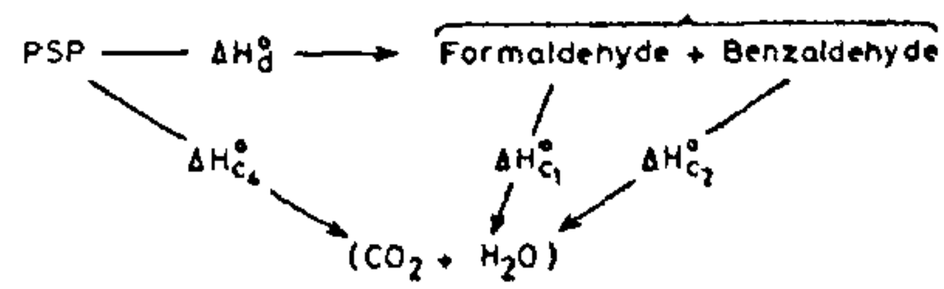
*Values are in kcal mol^{-1}, taken from refs. 6 and 7.
**Computed by group additivity method (ref. 22).



Scheme 1.

Pyrolysis gas chromatographic studies

It is known that polyperoxides degrade thermally to yield formaldehyde and an aldehyde or a ketone, depending on the vinyl monomer from which the polyperoxide is formed, i.e. an α-substituted or α-unsubstituted one. Staudinger[1] reported that benzophenone and formaldehyde are produced on thermal degradation of poly(diphenyletheylene peroxide); Bovey and Kolthoff[19], and Mayo and Miller[20] have reported that benzaldehyde and formaldehyde are the main products of PSP degradation. They have also reported some minor disproportionation products as well. The thermal degradation products of PSP were quantified by a pyrolysis gas chromatographic (PGC) study[21]. It was found that benzaldehyde and formaldehyde accounted for 90–95% of the total products. It was also found that there are some products other than these two which might be attributed to be the disproportionation products[20]. The decomposition pattern remains the same in the pyrolysis temperature range 100–450°C. Above this temperature, the pyrogram shows more peaks due to the further fragmentation of the primary degradation products. In the case of PMMAP too, a similar pattern of degradation was observed[7]. In PMMAP, the degradation products were methyl pyruvate and formaldehyde accounting for more than 95%, in the temperature range 150–350°C. The polyperoxides based on naphthalene were also found to exhibit a similar degradation pathway. PVNP2 at 90°C gives 2-naphthaldehyde and formaldehyde accounting for 98%. This polyperoxide being less stable, secondary



Scheme 2.

degradation sets in, at much lower temperatures. In the temperature range 150–350°C, the pyrolysis products of PMVNP1 and PMVNP2 were 1- and 2-acetonaphthone respectively, besides formaldehyde, accounting for 96% in each case.

Effect of additives

The degradation temperature of PSP, as observed by DSC, is altered in the presence of amines. The peak temperature at which the rate of degradation is maximal, depends upon the nature of the amines added to PSP before the reaction is started. The peak temperatures and pKa values of amines are given in Table 3; electron-donating groups promote degradation and the electron-withdrawing groups stabilize PSP. Further, the degradation temperatures of 3- and 4-substituted anilines appear to be related to their pKa values. The lowest degradation temperature with benzyl amine can be attributed to its high-pKa value. The degradation of PSP is sensitized by amines through the interaction of lone pair leading to the formation of imines. In the presence of amines, the degradation occurs by the usual free radical and ion-pair mechanism. A linear relationship is found to exist between PSP degradation peak temperature and the Hammet σ constants (Figure 6).

Nitroanilines, nitrobenzene, *p*-aminophenol, quinol and diphenyl amine are effective retardants of PSP degradation. The inhibition of *o*-aminophenol may be attributed to the least availability of lone pair for interaction with the peroxide due to its intermolecular hydrogen bonding. The effect of nitroamines is due to the interaction of the peroxides with NO_2 groups. During the PSP degradation, the radicals from PSP get stabilized through the formation of radical adduct with the help of the nitro groups. This inhibits propagation

Table 3. Decomposition peak temperature of PSP in the presence of amino compounds.

Sl. no.	Additive	DSC peak temperature (°C)	Change* in peak temp. with respect to PSP (°C)	pKa of amine
1.	Nil	121.5±0.2	—	—
2.	Aniline	97.5±0.2	−24.0	4.60
3.	4-Methyl aniline	97.0±0.2	−24.5	5.10
4.	3-Methyl aniline	92.5±0.2	−29.0	4.70
5.	*N*-Methyl aniline	96.3±0.2	−25.2	4.85
6.	Benzyl amine	85.0±0.2	−36.5	9.40
7.	3-Nitro aniline	146.3±0.3	+24.8	2.50
8.	4-Nitro aniline	162.5±0.4	+41.0	1.02
9.	Nitro benzene	157.5±0.2	+36.0	—
10.	4-amino benzoic acid	123.5±0.2	+ 2.0	4.90
11.	1,4-Diamino benzene	112.5±0.2	− 9.0	6.16
12.	2-Amino phenol	116.3±0.2	− 5.2	4.74
13.	Diphenyl amine	150.0±3.0	+28.5	0.90

*− indicates sensitization, + indicates desensitization.

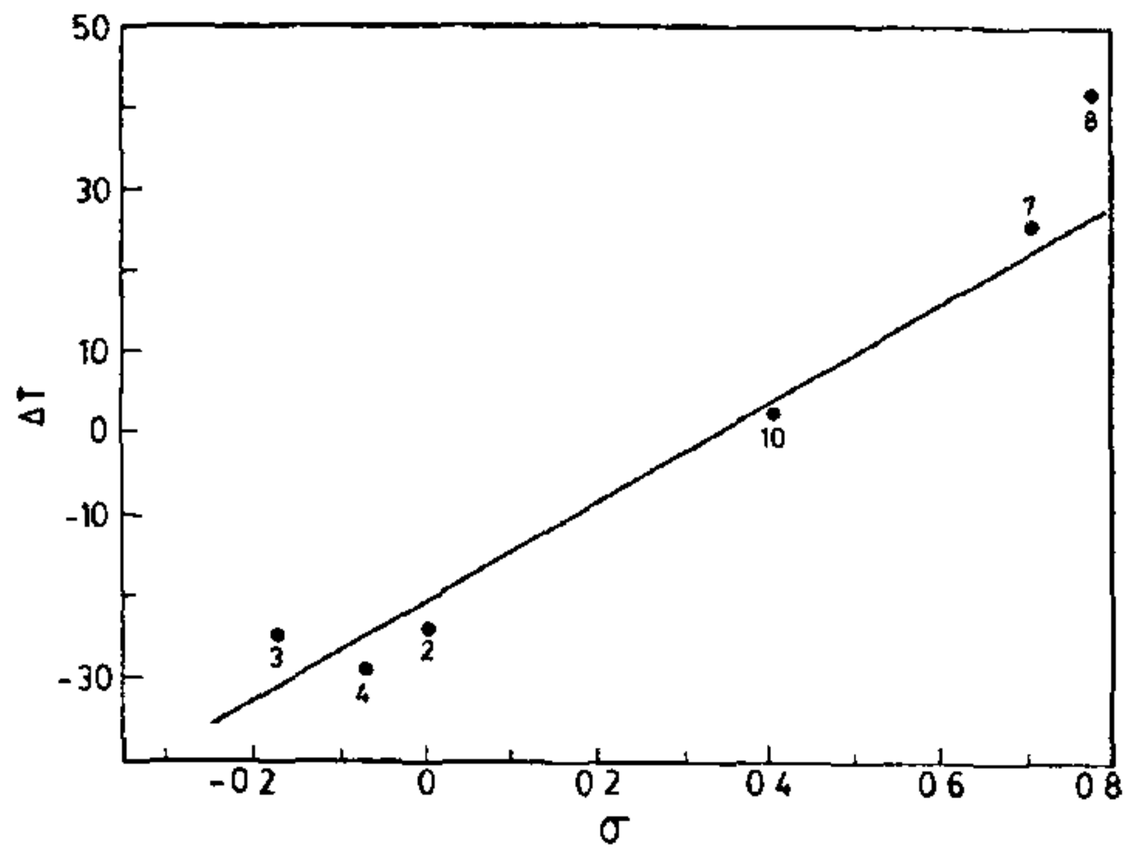


Figure 6. Plot of the difference in peak temperature (ΔT) against Hammett σ constants (numbering as in Table 3).

and consequently, the degradation shifts to higher temperatures. The retarding effect of diphenylamine may be due to its inhibiting action on the propagation step by the donation of a hydrogen atom from the amine to the radicals formed from PSP. The imine radical is stabilized by the phenyl groups through resonance, however, this does not occur with other amines.

Thermal degradation mechanism

The activation energy of polyperoxide degradation was found to be equivalent to the O–O bond dissociation energy. Hence, presuming an O–O bond scission as the rate-determining step, and involving the aldehydes or ketones and formaldehyde as the degradation products, a chain scission degradation mechanism for the thermal degradation of polyperoxides has been outlined (Figure 7). As already mentioned, apart from this, another pathway of degradation, viz. the disproportionation described by Mayo and Miller[20], yields minor products accounting for the rest of the total degradation products. For example, in PSP, it yields, α-hydroxyacetophenone, phenylglycol and phenylglyoxal as described in Scheme 3. The thermochemical calculations described earlier, substantiate this mechanism.

The unique phenomena of auto-pyrolysability and auto-combustibility in polymeric peroxide

During combustion the polymeric binder in a solid propellant fragments into smaller products. As mentioned earlier, PS/AP system also behaves similarly and gives a polymeric fragment containing an in-chain peroxy linkage (it was characterized to be PSP). This

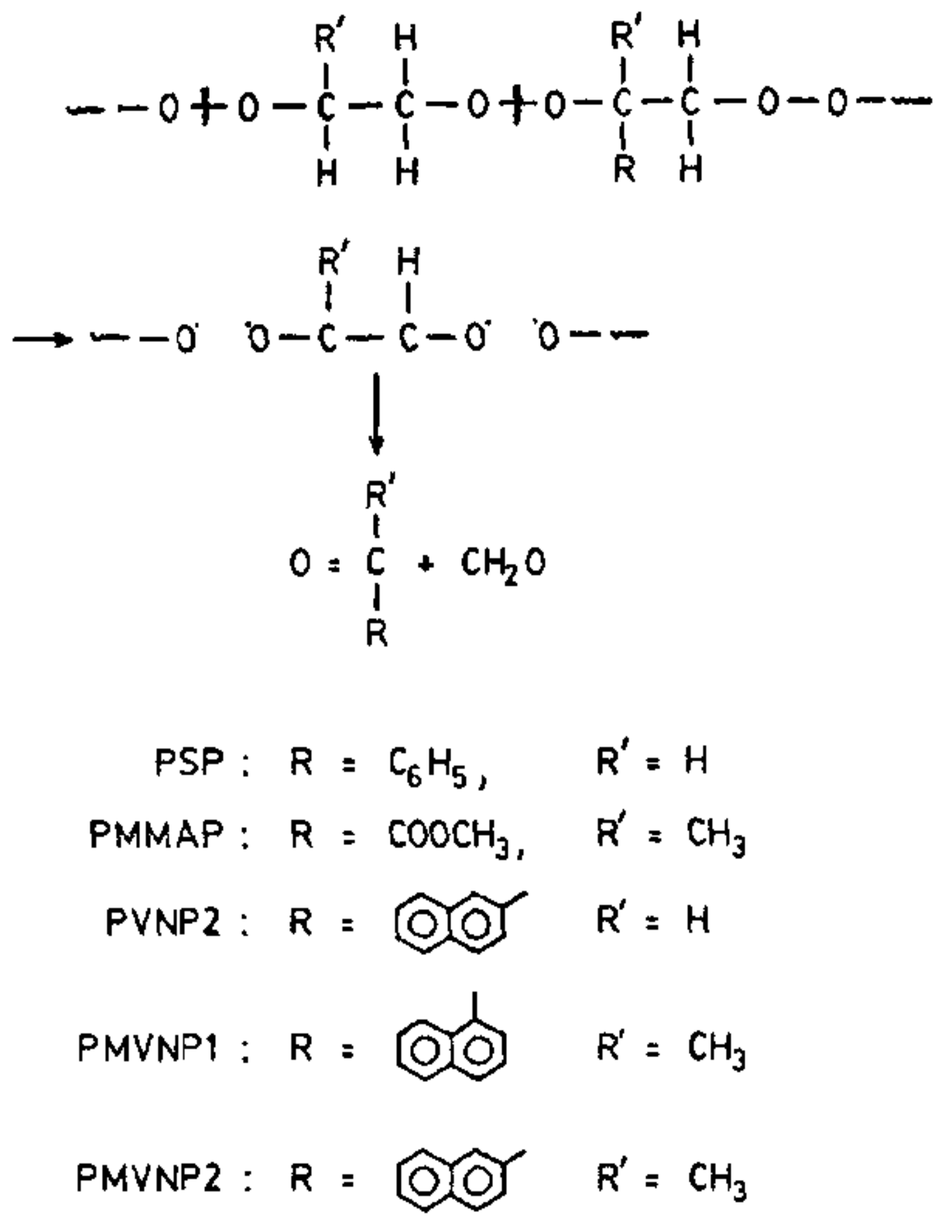
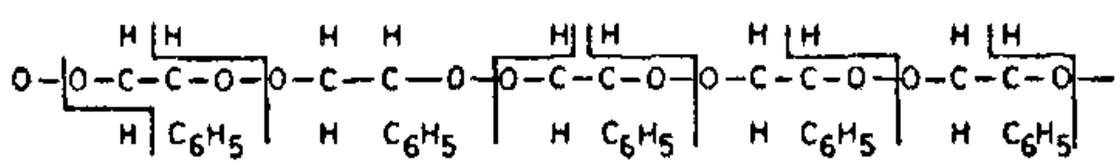


Figure 7. Degradation of polyperoxides.

observation called for further studies to look into how these peroxy-containing polymers are formed, degraded, etc. Heat of degradation data (experimentally obtained and thermochemically computed values) on PSP and PMMAP revealed that these peroxides underwent highly exothermic primary degradation.

Commonly polymers exhibit an endothermic degradation and demand a continuous supply of energy during their combustion. However, if a polymer can degrade sufficiently exothermically, it may support its own degradation (auto-pyrolysis) or its combustion. The highly exothermic degradation of PSP, gave us an indication that it might exhibit auto-pyrolysis. Interestingly, it was observed that once initiated, PSP not only sustains its own degradation but also supports a flame in air with a burning rate comparable to that of solid propellants. Such a fast-burning polymer, hitherto unknown, makes PSP an ideal candidate for a special fuel.

The auto-combustible behaviour of PSP was studied as described elsewhere[9]. The time-temperature profile showed a maximum gas temperature of 400°C, with an inflection point occurring at the gas–solid interface temperature (surface temperature). The enthalpy change for PSP going from ambient temperature to maximum gas temperature was found to be 45 kcal mol^{-1}.



Scheme 3.

Considering the losses, that occur during the combustion experiment, this value is in reasonable agreement with the experimentally measured (50 ± 1 kcal mol^{-1}) and thermochemically computed (50 ± 2 kcal mol^{-1}) ΔH_d^0's of PSP; i.e. the ΔH_d^0's of PSP during its combustion as well as in thermal degradation are the same. This suggests that the combustion of PSP occurs as a direct consequence of its degradation.

Experimentally obtained C_p values were used in the following equation to find out the rate of heat release during the combustion process.

$$\frac{dq}{dt} = C_p \frac{T_2 - T_1}{t_2 - t_1}, \tag{3}$$

where C_p is the heat capacity, T_2 and T_1 are the narrow temperature intervals in the profile, and t_2 and t_1 are the corresponding times, and dq/dt is the heat release rate. A computer simulated exotherm of the heat release (dq/dt) vs temperature was found to be identical with that obtained in the DSC experiment; the maximum of the simulated exotherm matches with the maximum of the DSC exotherm and the inflection point (surface temperature) on the profile (Figure 8). This also indicated that the combustion of PSP is controlled by its degradation. This conclusion is supported by the following facts: (i) The flame remains at the mouth of the tube, while the surface at which the degradation occurs recedes. (ii) Under controlled

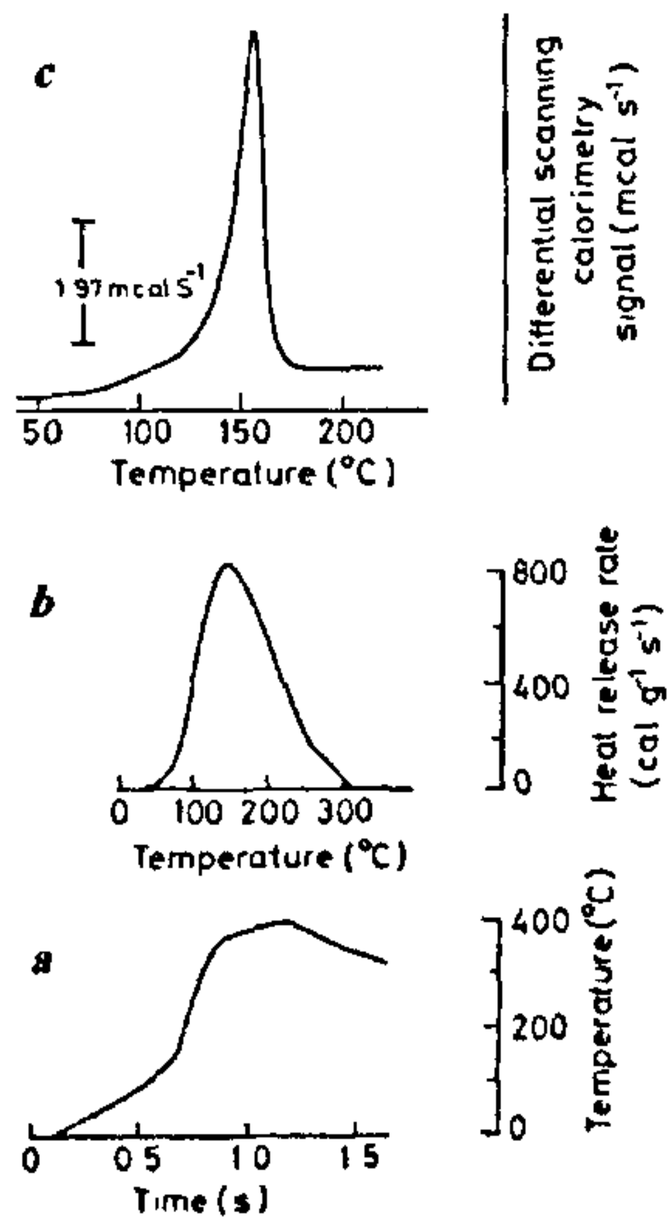


Figure 8. Thermal profile of PSP. **a**, Time-temperature trace during combustion. **b**, Computer-generated rate of heat release against time plot. **c**, DSC trace of degradation (heating rate 20°C min^{-1}; sample weight ~2 mg) (from ref. 9).

conditions. PSP degrade without a flame, the regression rate being equal to the burning rate. (iii) Two additives, viz. *p*-toluidine and nitrobenzene, which accelarates and decelerates respectively the degradation of PSP, was found to alter the burning rates in the same fashion during its combustion process.

Novel propellant formulation based on polyperoxides

The extremely fast-burning nature of the polyperoxides has paved way to the development of a novel propellant formulation based on them. For example, a new propellant system comprising PSP and AP has been developed. This formulation required only 30–35 wt% of the oxidizer (AP) for supporting its combustion, which in comparison with conventional propellant formulations (which require a minimum of 60–70 wt% AP) was drastically low, making the new system evidently fuel-rich. The burning rate of this composition showed some unexpected trends in the presence of the varying amounts of AP content to a level of 5 wt% where it peaked. It gradually decreased and finally levelled off at 30–35 wt% where the slurry started self-supporting its combustion. This observation was also supported by the results of DSC studies on these slurry compositions. Corresponding to the peak in burning rate vs AP content plot, there was a sensitization of about 10°C in the peak temperature of the degradation exotherm in the DSC studies. This peculiar behaviour has been attributed to AP acting as an additive in the initial stages and thereafter at the critical concentration in the role of conventional oxidizer.

Polyperoxide as initiator

Unlike in the case of organic peroxides, which are being extensively used as initiators and cross-linking agents, the polymeric peroxides have been less studied for these properties. Some of the recent reports, however, do make an attempt to use polymeric peroxides as initiators. They resort to the thermal degradation of the polyperoxides for generating free radicals.

Recently, it was reported from our laboratory that PSP in conjunction with amines could be used as initiators at room temperature for the radical polymerization of vinyl monomers[10]. PSP–diethylamine (DEA) and PSP–*N*,*N*-dimetheylaniline (DMA) systems were used. Styrene, methyl methacrylate and acrylamide were thus polymerized. The yields were low but better compared to benzoyl peroxide (BP)–DEA system at room temperature. It was found that polymerization takes place only when the PSP solution and DEA were added dropwise to the monomer. Addition of amine in one lot to PSP degraded the polyperoxide too fast that no polymerization occurred.

Conclusion

The present account gives an insight into the recent studies carried out to explore the physicochemical properties of polymeric peroxides. Though structurally similar to low-molecular weight dialkyl or diaryl peroxides, the 1:1 polymeric peroxides mentioned in this article show properties which could not have been predicted or extrapolated from the well-known physicochemical properties of the former class. The flexible nature of the polyperoxide chain segments and their conformations, the special thermochemistry and the highly exothermic nature of the primary degradation of these peroxides, their utility as a base for a highly fuel-rich propellant system, the capability of these peroxides as new class of initiators for vinyl polymerization etc. are only some of the new facets of the physics and chemistry of this class of polymers. Future studies directed towards exploring the properties of polymeric peroxides are likely be challenging and rewarding.

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