PERKIN 2

Study of alkyl radicals fragmentation from 2-alkyl-2-propoxyl radicals

Tomoyuki Nakamura,[a] Yasumasa Watanabe,[a] Shuji Suyama[a] and Hiroshi Tezuka *[b]

[a] *Fine Chemicals & Polymers Research Laboratory, NOF Corporation, 82 Nishimon, Taketoyo-cho, Chita-gun, Aichi-ken 470-2398, Japan*
[b] *Faculty of Liberal Arts, Shinshu University, Asahi, Matsumoto, Nagano-ken 390-8621, Japan*

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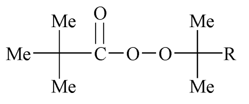
The reaction of a series of 2-alkyl-2-propoxyl radicals **2** in cumene has been studied. Alkoxyl radicals **2** were generated from the thermolysis of the corresponding *tert*-alkyl peroxypivalates, and underwent several modes of unimolecular reactions, that is, β-scission to give methyl radical, β-scission to give alkyl radicals and 1,5-H shift, which competed with hydrogen abstraction from cumene. The ratios of the rate constant for alkyl radicals elimination to that for methyl radical elimination, $k_\beta(\mathrm{R})/k_\beta(\mathrm{Me})$, were determined by using the radical trapping method employing TEMIO as the scavenger. The logarithm of the relative rate was satisfactorily correlated with the heat of formation of the leaving alkyl radicals containing the steric parameters of neopentyl radical **2d**. Then the plot of ln $[k_\beta(\mathrm{R})/k_\beta(\mathrm{Me})]$ *vs.* the SOMO energies of the corresponding alkyl radicals showed a linear relationship with a slope of -7.6 eV^{-1}, which is comparable to that of formolysis of alkyl bromides. The mechanism involving a fairly polar transition state of the alkyl radicals fragmentation from *tert*-alkoxyl radicals **2** is discussed in terms of the MO diagrams and the solvent effects.

Introduction

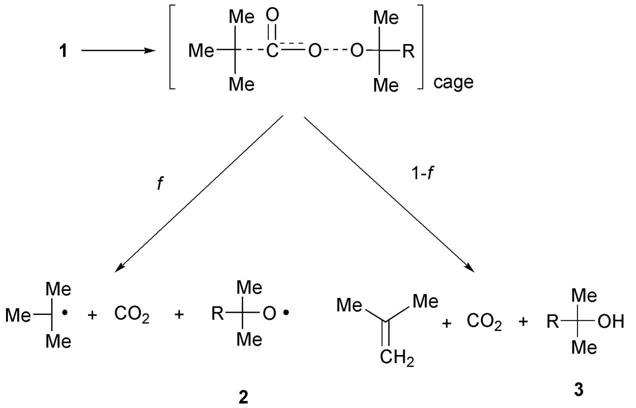
In free radical polymerisation, alkoxyl radical initiation can involve significant hydrogen abstraction from monomer, which can lead to a considerable proportion of unsaturated end groups in the resulting polymer.[1] Such end groups can have profound effects on the stability of the polymer towards thermal and/or photochemical degradation,[2] and hydrogen abstraction from polymer can cause polymer chain branching, which results in polymers with broad molecular weight distribution. Kamath and Sargent[3] have reported that *tert*-amyl peroxides are more efficient free radical initiators for the synthesis of acrylic high solids coating resins than conventional *tert*-butyl peroxide, because in contrast to *tert*-butoxyl radical, *tert*-amyloxyl ones readily undergo fragmentation (β-scission) to yield ethyl radicals that are poor in hydrogen abstraction ability. Then, the selective addition of ethyl radicals to monomers results in the production of polymers with narrow molecular weight distribution. We have reported the advantage of using *tert*-alkoxyl radicals of higher steric demand than *tert*-butoxyl and *tert*-amyloxyl radicals in free radical polymerisation of vinyl monomers such as styrene and methyl methacrylate.[4] Thus, an understanding of the structure–reactivity relationship for the initiating radical is quite important to synthesize desired polymers by a free-radical polymerisation process. From several studies[5–8,12] on the fragmentation of *tert*-alkoxyl radicals, it has been reported that the rate of β-scission of *tert*-alkoxyl radicals depends upon electron-donating polar effects of the substituents, besides the stability of the newly formed alkyl radicals. However, no good quantitative structure–reactivity relationship in the reaction has been illustrated.



$\mathrm{Me_3C{-}C({=}O){-}O{-}O{-}CMe_2R}$

1a-g

a : R = Me
b : R = Et
c : R = Pr^n
d : R = $\mathrm{CH_2CMe_3}$
e : R = Pr^i
f : R = $\mathrm{C_6H_{11}}^{cyclo}$
g : R = Bu^t



Scheme 1

2-Alkyl-2-propyl peroxypivalates **1** containing the respective groups of methyl (**1a**), ethyl (**1b**), *n*-propyl (**1c**), neopentyl (**1d**), isopropyl (**1e**), cyclohexyl (**1f**) and *tert*-butyl (**1g**) as the alkyl substituents were thermolysed in cumene. In the thermolysis of the peroxylesters **1** in cumene, a probable mechanism involving concerted two-bond scission within the solvent cage has been suggested depending on the quantitative investigation of the products, such as *tert*-butyl radical, $\mathrm{CO_2}$, and a *tert*-alkoxyl radical as shown in Scheme 1.[9,10] It was stoichiometrically revealed that the thermolysis of *tert*-alkyl peroxypivalates generates an equimolar amount of *tert*-butyl and *tert*-alkoxyl radicals outside the cage, and the β-scission rate of *tert*-alkoxyl radicals varies vastly along with the R group in *tert*-alkoxyl radicals.[10]

In the present work, for the further investigation of the behaviour of *tert*-alkoxyl radicals **2**, peroxylesters **1** have been used as a source of the radicals **2**, and an attempt to predict the

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Table 1 Relative yields of *tert*-alkoxyl radical-derived products in the thermal decomposition of 2-alkyl-2-propyl peroxypivalates **1** in cumene in the presence of TEMIO at 60 °C[a]

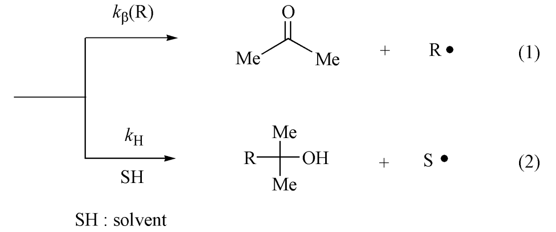
tert-Alkoxyl radicals	Relative product yields (%)					$[k_\beta(R)/k_H]^b$/M	$k_\beta(R)/k_\beta(Me)^b$ [= rel. $k_\beta(R)$]	ln [rel. $k_\beta(R)$]
	4	**5**	**6**	**7h**	**7i**			
2a	1.7	—		94.0	4.3	0.040[c]	≡1.0	0
2b	58.7	0.9		38.8	1.6	10.2	252	5.53
2c	32.8	0.6	43.3	22.4	0.8	9.9	254	5.50
2d	43.1	0.7	53.5	2.7	0.1	108	2.67×10^3	7.89
2e	94.5	0.5		4.8	0.2	132	3.30×10^3	8.10
2f	96.8	0.1	2.5	0.6	Trace	1130	2.80×10^4	10.24
2g	99.7	0.1		0.2	Trace	3490	8.64×10^4	11.37

[a] $[1]_0 = 0.040$ M, $[\text{TEMIO}]_0 = 0.040$ M, reaction time: 3.0 h. See ref. 10. [b] See text. [c] The corrected values for statistical factor.

structure–activity relationship in the fragmentation of *tert*-alkoxyl radicals is discussed on the basis of an MO diagram.

Results and discussion

It is known that the principal reaction paths available to *tert*-alkoxyl radicals **2** are β-scission to form alkyl radicals and acetone, and hydrogen abstraction from solvent leading to the corresponding 2-alkylpropan-2-ols (Scheme 2). So far, the ratio



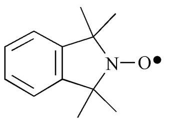
Scheme 2

of the yield of acetone to that of 2-alkylpropan-2-ols has been used as an index of the relative reactivity of the fragmentation to the hydrogen abstraction of *tert*-alkoxyl radicals **2**.[7] However, in the thermolysis of **1**, 2-alkylpropan-2-ols are also formed in the solvent cage as shown in Scheme 1, and an appreciable extent of cage reaction is expected (*ca.* 50%).[9d,10] Therefore, the above relative reactivity cannot be precisely estimated on the basis of the yields of acetone and 2-alkylpropan-2-ols.

Then, the relative reactivity of *tert*-alkoxyl radicals **2** toward the fragmentation and to the hydrogen abstraction was estimated based on the results from the radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl-oxyl (TEMIO, abbreviated to T) as a scavenger.[10,11] Thus, 2-alkyl-2-propyl peroxypivalates **1** (0.040 M) were thermolysed in the presence of TEMIO (0.040 M) in degassed cumene at 60 °C for 3.0 h. The various alkoxylamines were obtained from the respective precursor radicals. That is, alkoxylamines **4** were obtained from the corresponding alkyl radicals generated from β-scission of **2**, accompanied by the formation of alkoxylamine **5** derived from methyl radical formed by the alternative β-scission of **2**. Alkoxylamines **6** were obtained from the intramolecular hydrogen transferred radicals of **2**. Alkoxylamines **7h** and **7i** were formed from cumyl radicals generated in the intermolecular hydrogen abstraction from cumene by *tert*-alkoxyl radicals **2**. The relative yields of the alkoxyl radical-derived alkoxylamines are summarised in Table 1.

An estimation of the reactivity of *tert*-alkoxyl radicals toward the fragmentation

The relative reactivity of the fragmentation to the hydrogen abstraction for each of the *tert*-alkoxyl radicals **2**, $k_\beta(R)/k_H$, is proportional to the relative yield of **4** toward **7** (*i.e.*, **7h** and **7i**) as shown in eqn. (3),

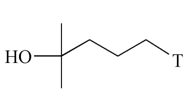


R—T

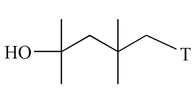
a : R = Me (= **5**)
b : R = Et
c : R = Pr^n
d : R = CH_2CMe_3
e : R = Pr^i
f : R = $C_6H_{11}^{cyclo}$
g : R = Bu^t

4a-g

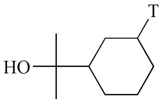
TEMIO = T



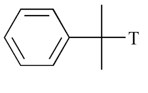
6c



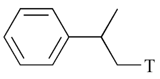
6d



6 f



7h



7i

$$\frac{k_\beta(R)}{k_H} = \frac{[\mathbf{4}]}{[\mathbf{7}]}[SH] \qquad (3)$$

where k_β(R) is the rate constant for the alkyl radical fragmentation of *tert*-alkoxyl radicals **2**, k_H is the overall rate constant for hydrogen abstraction by *tert*-alkoxyl radicals **2** from cumene, and [SH] is the concentration of solvent. The values of $k_\beta(R)/k_H$ for each alkoxyl radical were obtained by taking [SH] = 7 mol dm^{-3}. It can be seen from Table 1 that the values of $k_\beta(R)/k_H$ increased in the order of R = methyl < ethyl ~ *n*-propyl < neopentyl < isopropyl < cyclohexyl < *tert*-butyl.

Assuming that the value of k_H is approximately constant for each alkoxyl radical,[7,13] the relative reactivity of *tert*-alkoxyl radicals to *tert*-butoxyl radical **2a** toward the alkyl radical fragmentation, $k_\beta(R)/k_\beta(Me)$, was obtained as the relative value of $k_\beta(R)/k_H$ for **2** to that of **2a**.

The correlation of the relative reactivity of the fragmentation with the stability of alkyl radicals

Kochi has mentioned that the rates for β-scission are attributed to the stability of the leaving alkyl radicals.[5] The stabilisation energy of short-lived radicals (half lives less than 10^{-3} s) can be correlated with the difference between the heat of formation of alkyl radicals and that of the parent hydrocarbons.[14] That is, the value of $[\Delta H(R^\bullet) - \Delta H(RH)]$ is used as a criterion of the alkyl radical stability. Then, the heat of formation, $[\Delta H(R^\bullet)]$, of alkyl radicals was calculated for several stable conformations by using a semi-empirical AM1 method, and the minimum value of energy was adopted. The SOMO energies of alkyl radicals $[E_{SOMO}(R^\bullet)]$ were also calculated and the results of the calculations are tabulated along with the observed values for the heat of formation of alkyl radicals (Table 2).

The plot of the calculated values *vs.* the observed values[15] of $\Delta H(R^\bullet)$ gave a fairly good straight line as illustrated in Fig. 1. In addition, it can be seen from Fig. 2 that the negative values of the calculated SOMO energies are proportional to the observed

Table 2 Thermochemistry of alkyl radicals R$^\bullet$

Alkyl radicals	$\Delta H_{obsd}(R^\bullet)^a$/kcal mol^{-1}	$\Delta H_{calc}(R^\bullet)^b$/kcal mol^{-1}	$\Delta H_{obsd}(R^\bullet) - \Delta H_{obsd}(RH)$/kcal mol^{-1}	$E_{SOMO}(R^\bullet)^c$/eV	IP^d/eV
Me	34.4	31.3	52.2	−9.886	9.86
Et	28.0	18.2	48.1	−9.211	8.78
Pr^n	21.8	12.2	46	−9.322	8.69
CH_2CMe_3	8.7	5.08	48.7	−9.302	8.33
Pr^i	19.2	6.77	44.2	−8.795	7.9
$C_6H_{11}{}^{cyclo}$	13.9	−6.25	43.4	−8.758	7.66
Bu^t	9.4	−2.7	41.5	−8.476	7.07
$PhCH_2$	47.8	52.0	35.8	−8.683	7.76

[a] The observed value of heat of formation for alkyl radicals, ref. 15. [b] The calculated value of heat of formation for alkyl radicals at the RHF/AM1 level. [c] The SOMO energies of alkyl radicals calculated at the UHF/AM1 level. [d] Ionisation potential of alkyl radicals, ref. 16.

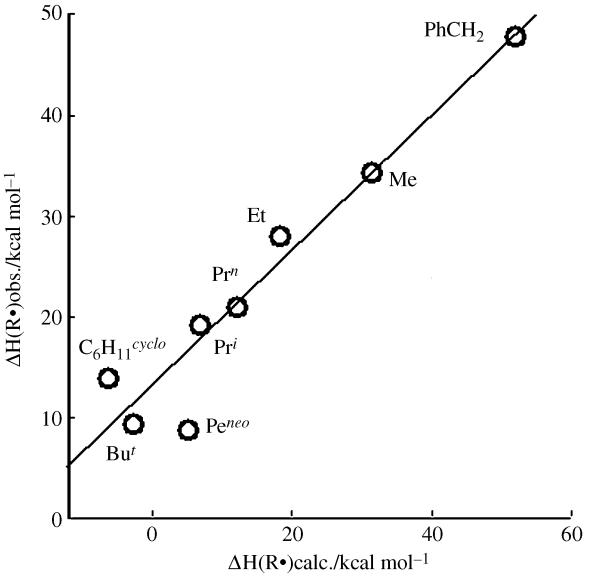


Fig. 1 The plot of the observed values *vs.* the calculated values of the heats of formation for the alkyl radicals.

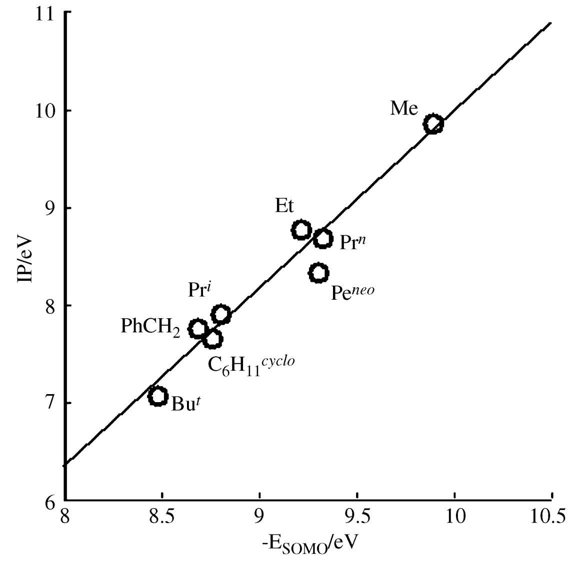


Fig. 2 The correlation of the ionisation potentials with the negative values of the SOMO energies of the alkyl radicals.

values of ionisation potential (IP),[16] which is consistent with Koopmans theory.[17] Good agreements of the calculated values with those observed suggest the semi-empirical AM1 method to be reliable to this extent.

Here, the observed values of both $\Delta H(R^\bullet)$ and $\Delta H(RH)$ are employed in the following discussion of the mechanism.

The reactivity of the fragmentation of *tert*-alkoxyl radicals appears to depend upon the stability of the leaving alkyl radicals as shown in Table 2. This is qualitatively consistent with the results previously reported,[5,6,12] and the plot of the logarithm of $k_\beta(R)/k_\beta(Me)$ *vs.* the stability of alkyl radicals, $[\Delta H(R^\bullet) - \Delta H(RH)]$, gave a good correlation except for R = Pe^{neo} as shown in Fig. 3.

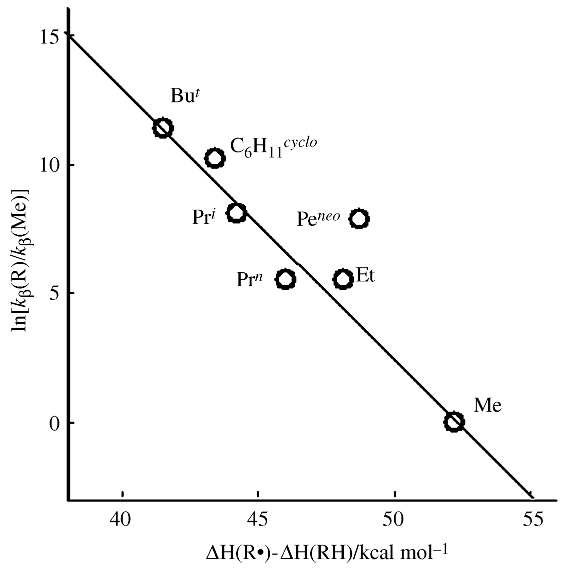


Fig. 3 The plot of the reactivity of 2-alkyl-2-propoxyl radicals **2** in the fragmentation *vs.* the relative heat of formation of the alkyl radicals.

The upward deviation of the 4,4-dimethyl-2-methyl-2-pentoxyl radical **2d** implies steric effects on the fragmentation in Fig. 3. The steric strain of an alkyl group R in *tert*-alkoxyl radicals **2**, $E_{st}(R)$, was approximated with that of the corresponding *tert*-alkyl alcohol **3** because of the negligible size of an alcoholic hydrogen, and it was estimated with MM2 calculations (Table 3).[18] The bulky effects in the *tert*-alkyl alcohols **3**, which signify those of *tert*-alkoxyl radicals **2**, were evaluated as the difference between the strain energy of the 2-alkylpropan-2-ol, $RC(Me)_2OH$ **3** and that of RH, in order to eliminate the inherent intramolecular strain energy of alkyl radical, R$^\bullet$. For example, 2-cyclohexylpropan-2-ol has the steric energy, 10.20 kcal mol^{-1}, but since cyclohexane has a fairly large intramolecular strain, 6.55 kcal mol^{-1}, due to its atom connectivities, the steric effect of cyclohexyl group was estimated to be 3.65 kcal mol^{-1} (*i.e.*, 10.20 − 6.55). The steric effects are described in the relative values for R in *tert*-alkoxyl radicals **2** to methyl group in Table 3. The steric strain energies of MeOH and *t*-BuOH are 0.05 and 2.99 kcal mol^{-1} by virtue of MM2 calculations.[18] The difference of the strain energy is approximately 3 kcal mol^{-1} in the above *tert*-butyl alcohol and methanol. It can concurrently be the difference of those of *tert*-butoxyl and methoxyl radicals. In spite of the small values of those in the other radicals (less than 4 kcal mol^{-1}), the strain energies of both 4,4-dimethyl-2-methyl-2-pentoxyl and 3,3-dimethyl-2-methyl-2-butoxyl radicals are significantly higher, *i.e.*, 7.26 and

Table 3 Thermochemistry of 2-alkyl-2-propoxyl radicals **2** [RC(Me)$_2$O$^•$]

R in **2**	$\Delta H(\mathbf{2}) - \Delta H(\mathbf{3})^a$/kcal mol^{-1}	$E_{\text{SOMO}}(\mathbf{2})^b$/eV	$E_{\text{st}}(\text{R})^c$/kcal mol^{-1}
Me	58.88	10.80	0
Et	58.56	10.65	1.86
Pr^n	58.87	10.67	1.85
CH$_2$CMe$_3$	58.11	10.63	7.26
Pr^i	58.29	10.53	3.74
C$_6$H$_{11}$^{cyclo}	59.85	10.46	3.65
Bu^t	58.86	10.44	6.09

[a] The heat of formation of both *tert*-alkoxyl radicals and *tert*-alkyl alcohols was estimated at the RHF/AM1 level. [b] The SOMO energies of the *tert*-alkoxyl radicals calculated at the UHF/AM1 level. [c] The relative strain energies of the corresponding *tert*-alkyl alcohols estimated by using the Spartan MM2 traded by Wavefunction, Inc. The steric effects of R in the *tert*-alkoxyl radicals were estimated as the difference of the strain energy of the RC(Me)$_2$OH and that of the corresponding RH, *e.g.*, 10.20 − 6.55 = 3.65 kcal mol^{-1} in the cyclohexyl group.

Table 4 The interatomic distances less than those of the van der Waals radii^a in the optimised conformers **8** and **9** at the RHF/AM1 level of both 4,4-dimethyl-2-methyl-2-pentoxyl radical (**2d**) and 3,3-dimethyl-2-methyl-2-butoxyl radical (**2g**)

Interatomic distance/Å in **8**		Interatomic distance/Å in **9**^{b}	
H_3C_9	2.49	H_6H_{23}	2.131
H_8H_{22}	1.98	H_8H_{14}	2.040
$H_{26}O_{13}$	2.18	$H_{10}H_{22}$	2.072
		$H_{11}H_{19}$	2.188

[a] The sum of the van der Waals radii of two hydrogens, the sum of those of hydrogen and oxygen, and the sum of those of hydrogen and carbon are 2.40, 2.49 and 2.90 Å, respectively.[15c,d] [b] The interatomic distances of $H_{18}O_{13}$ and H_4O_{13} (shorter ones) in **9** are 2.516 and 2.502 Å, respectively.

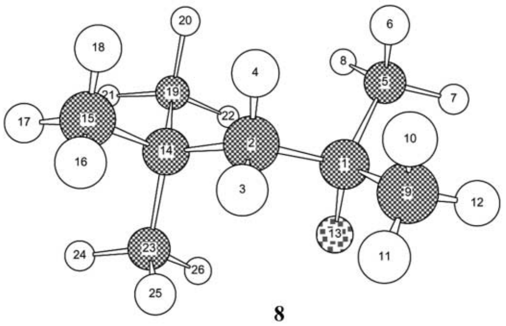
6.09 kcal mol^{-1} on the basis of methyl group respectively as shown in Table 3.

The steric acceleration of the fragmentation can result from either the back strain of the *tert*-alkoxyl radicals **2** or the depression of hydrogen abstraction competing with fragmentation. Although the steric strain energy of R = *t*-Bu is by no means inferior to that of R = neopentyl as shown in Table 3, the upward deviation is observed exclusively at R = neopentyl. Therefore, the steric acceleration of the fragmentation should not be ascribed to the back strain of the *tert*-alkoxyl radicals **2**.

In hydrogen abstraction, no steric size effects of attacking species are usually observed, *e.g.*, the hydrogen abstraction rates by such different radicals as MeO$^•$ and *t*-BuO$^•$ from methanol are approximately equivalent as follows:[13] $k_{\text{MeO}} = 2.63 \times 10^5$ dm^3 mol^{-1} s^{-1} and $k_{t\text{-BuO}} = 2.9 \times 10^5$ dm^3 mol^{-1} s^{-1}. In the present study, also, the mechansm has been discussed on the assumption that the hydrogen abstraction rates are constant irrespective of the attacking *tert*-alkoxyl radicals.

However, in the optimised conformer **8** for 4,4-dimethyl-2-methyl-2-pentoxyl radical (**2d**), the close contacts are observed in the front of the oxygen radical center, such as $O_{13}H_{26}$, while in the optimised one **9** for 3,3-dimethyl-2-methyl-2-butoxyl radical (**2g**), the close contacts in the interatomic distances are produced in the backside of the oxygen radical center, such as H_6H_{23}, H_8H_{14}, $H_{10}H_{22}$ and $H_{11}H_{19}$ as shown in Table 4.

Therefore, the γ-carbon methyl groups are expected effectively to shield the oxygen radical center in the optimised 4,4-dimethyl-2-methyl-2-pentoxyl radical **8** and this may disturb the intermolecular hydrogen abstraction,[4d,10,19] resulting in the relative enhancement of the fragmentation. On the other hand, the β-carbon methyl group may not screen the oxyl radical center effectively in the 3,3-dimethyl-2-methyl-2-butoxyl radical **9**.



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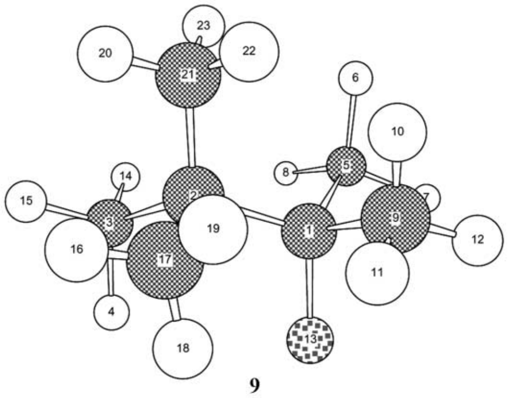


9

A significant intramolecular 1,5-hydrogen transfer was really observed in the 4,4-dimethyl-2-methyl-2-pentoxyl radical (**2d**) as shown in Table 1. A 1,5-hydrogen transfer in the 4,4-dimethyl-2-methyl-2-pentoxyl radical (**2d**) has a 3-fold statistical advantage over that in the 2-methyl-2-pentoxyl radical (**2c**). However, the rates for the intramolecular 1,5-hydrogen transfer are considered to be comparable for both alkoxyl radicals because of the relatively unstable chair conformation of the six-membered ring transition state in **2d** as a result of the steric repulsion between the two methyl groups attached to the α- and γ-carbons.[10] It is reasonably assumed that the intermolecular hydrogen abstraction is retarded due to the steric hindrance of attacking radicals exclusively in 4,4-dimethyl-2-methyl-2-pentoxyl radical. The reactivity of the β-scission of 4,4-dimethyl-2-methyl-2-pentoxyl radical is modified based on the above interpretation, resulting in the eqn. (4).

$$\ln [k_\beta(\text{R})/k_\beta(\text{Me})] = 59 - 1.13[\Delta H(\text{R}^•) - \Delta H(\text{RH})] + 0.59E_{\text{st}}(\text{R}) \quad (4)$$

In eqn. (4), a third term is included in compensation for the deviation of the hydrogen abstraction rate. The coefficients of both [$\Delta H(\text{R}^•) - \Delta H(\text{RH})$] and $E_{\text{st}}(\text{R})$ were determined by means of multiple regression analysis. The correlation is much more improved as shown in Fig. 4. It indicates that the reactivity of the fragmentation is proportional to the relative values of heat of formation of the alkyl radicals formed. However, the eqn. (4) seems to apply only to simple aliphatic radicals and most of the studies presented are efforts to explain and include the neopentyl case in the correlation.

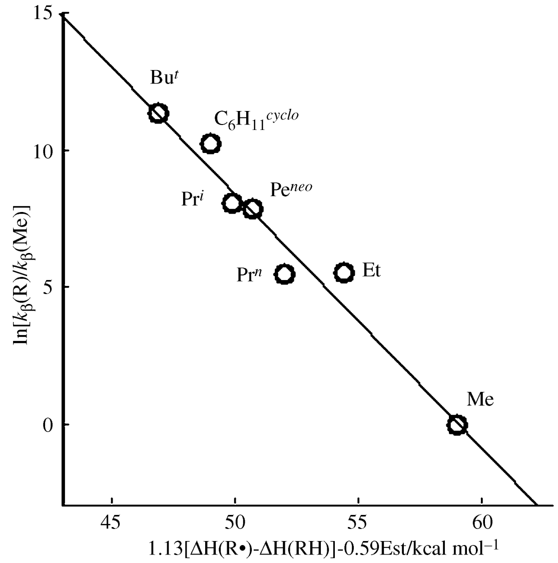


Fig. 4 The plots of the reactivity of *tert*-alkoxyl radicals toward the fragmentation *vs.* the relative heat of formation of the alkyl radicals. The value of Pe^{neo} is only modified for steric strain energy, E_{st}.

The relationships obtained in this work should be useful for the prediction of the relative reactivity in the fragmentation of the new *tert*-alkoxyl radicals developed as the precursors of new initiators for free radical polymerisation.

The calculation of the stability of *tert*-alkoxyl radicals

Similarly to the case of alkyl radicals, the thermochemical properties and the SOMO energies for *tert*-alkoxyl radicals **2**, E_{SOMO}(**2**), are listed in Table 3. The difference between the heat of formation of *tert*-alkoxyl radicals **2** and that of the corresponding alcohols **3**, [ΔH(**2**) − ΔH(**3**)], which compensates the inherent bond energies contained in the respective radicals, can be used as a criterion of the stability of *tert*-alkoxyl radicals.

From Table 3, it is clearly shown that both the values of [ΔH(**2**) − ΔH(**3**)] and those of E_{SOMO} were almost identical for each *tert*-alkoxyl radical **2**, indicating little contribution of *tert*-alkoxyl radical stability to the reactivity of the fragmentation.

The transition state in the fragmentation of *tert*-alkoxyl radicals

As above, the reactivity of the fragmentation is controlled by the stability of the alkyl radicals eliminated, and it is independent of the stability of *tert*-alkoxyl radicals **2**. The fragmentation is also exothermic, at least more than 5 kcal mol^{-1} based on the heats of formation of *tert*-alkoxyl radicals **2**, alkyl radicals formed and acetone. Since the formation reaction of the alkyl radicals is endothermic, the driving force of the fragmentation would be the stabilising energy provided by the formation of the carbonyl double bond of acetone.

The above fact suggests that the transition state is similar to the initial state. Hence, the odd electron would principally be inclined to localise on the acetone moiety, instead of the alkyl moiety departing in the transition state. In order to study a detail of the transition state of the fragmentation, the correlation of the SOMO energies of the leaving alkyl radicals to the relative rate of the fragmentation was evaluated. Then it can be seen from Fig. 5 that the plot of the logarithm of k_β(R)/k_β(Me) *vs.* the SOMO energies of the leaving alkyl radicals gave a fairly good straight line with a slope of −7.6 eV^{-1}. In formolysis of alkyl bromides,[20] RBr (R = Me, Et, Pr^i, Bu^t), which is known as an S_N1 type reaction, the similar plot of ln [k_{RBr}/k_{MeBr}] *vs.* the SOMO energies of the alkyl radicals was overlayed on Fig. 5. Since the solvolysis of *tert*-butyl bromide is enhanced not only by the alkyl cation stability but also by the back strain, no good linear relation is obtained. However, the slope may roughly be comparable to that of the fragmentation. It indicates that the SOMO energy has an effect on the formation of the alkyl cation corresponding to the leaving alkyl radicals in the β-scission.

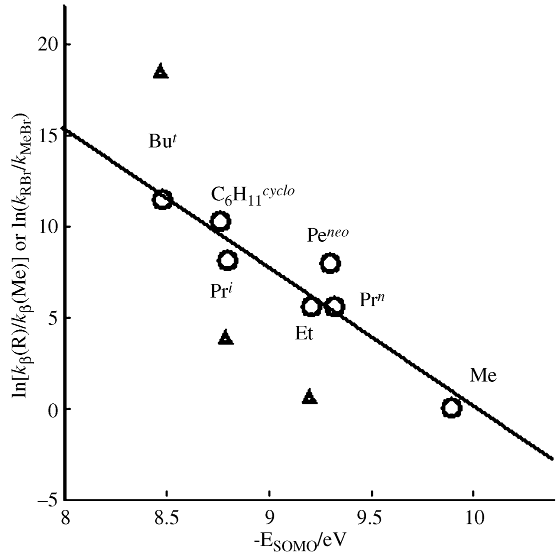
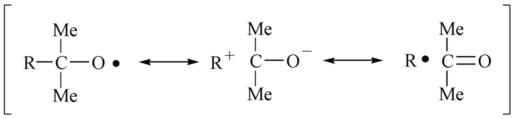


Fig. 5 The plots of the reactivity in the fragmentation of the *tert*-alkoxyl radicals and the plots of the relative reactivity in the formolysis of alkyl bromides *vs.* the negative values of the SOMO energies of the alkyl radicals formed. ○: The reactivity in the fragmentation of the *tert*-alkoxyl radicals. Δ: The relative solvolysis rates of alkyl bromides.

Therefore, the fragmentation reactivity will also be controlled considerably by the stability of the alkyl cation besides the radical stability. The polar transition structure in the fragmentation is more favourable in a polar solvent such as cumene, while the solvation is supposed to affect little the competitive hydrogen abstraction.[8] The above phenomenon is consistent qualitatively with the results reported before.[6–8,12] It is expressed in terms of the resonance form as follows:



$$\left[\mathrm{R{-}\overset{Me}{\underset{Me}{C}}{-}O\bullet} \longleftrightarrow \mathrm{R^{+}\ \overset{Me}{\underset{Me}{C}}{-}O^{-}} \longleftrightarrow \mathrm{R\bullet\ \overset{Me}{\underset{Me}{C}}{=}O} \right]$$

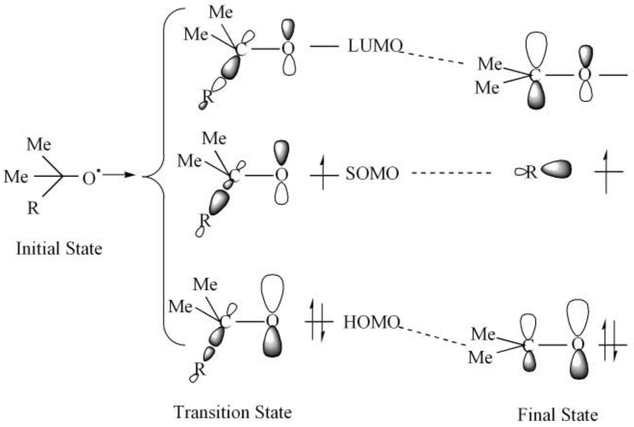
The reaction mechanism is satisfactorily elucidated by means of the above polar resonance form. However, on the analogy of the orbital mode of 2-oxoethyl radical, the transition state may qualitatively be illustrated in terms of the similar three electrons system as shown in Scheme 3.[21] The HOMO, LUMO and SOMO in the transition state may be converted to π,π* orbitals in the acetone and n orbital in the alkyl radical, respectively. The orbital lobe in the SOMO of oxygen is considered to be a little large, so the odd electron is inclined to localise on the oxygen atom fairly in view of the results in Fig. 5. It may result in an electron deficient alkyl moiety and an electron rich acetone moiety in the transition state.

Davies observed the acceleration by trifluoroacetic acid in the fragmentation of *tert*-alkoxyl radicals and he reasonably explained it by the decrease of the interaction between the SOMO of the alkyl radical eliminated and the HOMO of the resulting carbonyl compound.[22] In the present case, the polar transition state in a polar solvent such as cumene is explained by means of SOMO–LUMO interaction in the alkyl radical and acetone formed.

Experimental

General

Cumene was purified by distillation after washing with concentrated sulfuric acid. TEMIO was prepared by the literature procedure.



Scheme 3

Procedure for the thermolysis

A 2 ml solution of *tert*-alkyl peroxypivalate (0.05 M) in cumene was charged into a glass ampoule. The ampoule was purged with nitrogen, sealed, and immersed in a constant temperature bath regulated at 60 °C.

Theoretical methods

The AM1 method was employed to calculate the molecular orbital energies and the heat of formation of the alkyl and *tert*-alkoxyl radicals, because the better results were obtained with the AM1 method rather than the PM3 one for radicals. The radicals were estimated with UHF optimisation for the SOMO energies. The RHF method was used for the heat of formation in order to obtain the energies on the same scale as that for the closed-shell molecules.[23,24] The Spartan MM2 method traded by Wavefunction, Inc. was used for molecular mechanics calculations of the *tert*-alkyl alcohols. The radicals were calculated for several possible conformations. The conformation that results in the minimum value of energies was adopted. Vibrational frequencies for the radicals were calculated to ensure that a minimum energy geometry was reached. The conformations and configurations of the radicals were analysed with Toray 3D-MOL and CS Chem3D Pro.

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