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Quantum Chemical Rationale on Free-Radical Formation of Irradiated Acrylic Polymers

Akihiro Noguchi, Shin-ichi Kondo, and Masayuki Kuzuya*
Laboratory of Pharmaceutical Physical Chemistry, Gifu Pharmaceutical University, 5-6-1, Mitahora-higashi, Gifu 502

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The bond cleavage of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) in their excited states was investigated by means of molecular orbital calculations (AM1 and INDO/S-CI methods) using model molecules. The calculated reaction potentials for the bond cleavages in the excited states showed that the most dissociative bonds are the α-C–H bond for PAA and the C–C bond associated with the decarboxylation for PMAA. β-C–C bond cleavage following the above-mentioned side-bond cleavages seems to be feasible in the higher excited states. The formation of free radicals in the plasma- and γ-irradiations of PAA, PMAA, and their esters could be well explained as reactions in the excited states.

A number of ESR studies have been reported concerning radicals formed by various types of radiation, such as γ-, X-, and UV-irradiation, in poly(methacrylic acid) (PMAA), poly(acrylic acid) (PAA), and their esters.[1—24] The formation of various free radicals and several kinds of mechanisms for the formation have been reported in such studies. We have recently reported on a detailed ESR study of the free-radical formation and decay of plasma-irradiated PMAA and its esters, showing the presence of midchain and monomer-derived radicals, in addition to the terminating radicals in a plasma-irradiated polymer. Also, the mechanism by which the radicals were formed was deduced on the basis of ESR kinetics and its spectral simulation.[25,26]

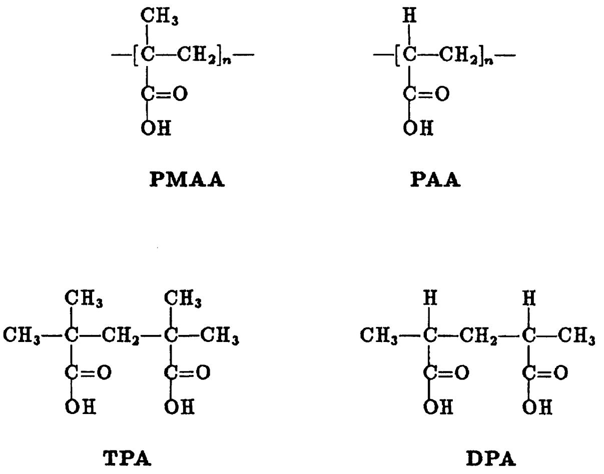
γ- and plasma-irradiation can generate ionized molecules together with excited molecules; the excited states are known to play an important role in the radiolysis of polymers.[21—24] However, the detailed nature of the excited states of PMAA and PAA has not been considered.

In this study, in order to gain a theoretical basis concerning radical formation, we investigated the nature of the bond cleavages of non-ionized PMAA and PAA in excited states by means of molecular orbital (MO) calculations using model compounds.

Calculation

2,2,4,4-Tetramethyl- (TPA) and 2,4-dimethylpentanedioic acids (DPA) were used as model compounds for PMAA and PAA, respectively. Also, acetic acid and its methyl ester were used as model compounds for an investigation of the nature of bond cleavage in the carboxyl moiety (Scheme 1).

The MNDO (modified neglect of diatomic orbital) semiempirical MO method[27] with a 3×3 CI (configuration interaction) has been proven to give good results concerning bond dissociation and radical–radical recombination reaction paths in the ground state.[28] The AM1 (Austin Model 1) method,[29] a revised method of the MNDO method, with a 3×3 CI seems to give more accurate results.[30] However, the method generally accompanies some difficulties concerning the excited state, such as a restriction on the number of MO's incorporated into the CI treatment and the selection of the MO's used to construct the CI function, though some successful results have been obtained for reactions in the excited states.[31,32] Also, the method has a tendency to overestimate the stability of the excited state.[32,33] It therefore seems to be inadequate for an examination of the reaction potential in the excited state, since the calculated reaction potential of the excited state may depend exceedingly on that of the ground state.



PMAA **PAA** **TPA** **DPA**

Scheme 1.

Thus, the potential energies of the excited state were calculated as a sum of the heats of formation of the ground state calculated by the AM1 method with a 3×3 CI and the transition energies calculated by the INDO/S-CI method, which is known to well reproduce the transition energies for a variety of molecules. We believe that this method gives qualitatively correct results, although the calculated reaction potentials in the excited states are not based on the relaxed geometries in those states.

The bond-dissociations in the ground state were examined by means of the AM1 method with a 3×3 CI, in which the bond length concerned with the cleavage was spanned in steps of 0.2 Å over the range from the length near the equilibrium to 3.0 Å; the geometries at each point along the reaction path were optimized for the moiety involving two atoms successively attached to the dissociating bond. INDO/S-CI calculations of the excited states were carried out by the method and parameters for saturated molecules by Salahub[34] using the AM1 geometries calculated above.

The reaction potentials of the β-cleavage in radicals formed by decarboxylation in TPA and by α-hydrogen abstraction in DPA were estimated from the potentials in the ground state calculated by the UHF-AM1 method and the transition energies by the INDO/S-CI method, in the same manner as above (Scheme 2).

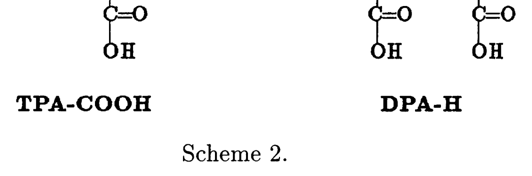
The calculations were carried out on a FACOM M-780/20 computer at the Computation Center of Nagoya University and on a HITAC M680-H computer at the Computer Center of the Institute for Molecular Science, Okazaki.

Results and Discussion

The INDO/S calculation well reproduced the experimentally known singlet–singlet transition energies for acetic acid,[35] as shown in Table 1. The calculated lowest singlet–singlet ($n\rightarrow\pi^*$) transition energies of polymer model compounds, TPA and DPA, were slightly higher (0.3—0.4 eV) than that of acetic acid (Table 2).

Bond Cleavages in Excited States. The relationships between the radiation effect and the chemical structure in vinyl polymers are known as the Millar–Wall–Charlesby empirical rule.[36—39] This rule shows that vinyl polymers with two side chains attached to a single carbon degrade, whereas those with a single side chain or no side chain crosslink. Tsuda et al. have investigated the potential curves of the bond cleavages in simple aliphatic molecules by the MNDO and INDO/S methods and attributed the nature of the rule to the shape of the adiabatic potential curve in the ground state.[40]

It has been known that the major radical formed by the plasma- and γ-irradiation of PMAA is the terminating radical. PMAA is a degradable polymer in the chemical structure, based on the Millar–Wall–Charlesby empirical rule. We have suggested, in an ESR kinetic study of free-radical formation in plasma-irradiated PMAA and its esters, that the main-chain scission is due to a β-elimination following decarboxylation, and not due to a direct reaction caused by irradiation.[25,26] A mechanism similar to that mentioned above has also been suggested in studies of γ-irradiated PMAA and its methyl ester.[20,21] On the other hand, studies of γ-irradiated PAA have shown that the major radical formed by irradiation is a midchain radical formed by α-hydrogen abstraction.[18,21—24] Decarboxylation as an initial step on the irradiation of PAA has been reported only by Hill et al.[23]



TPA-COOH **DPA-H**

Scheme 2.

The midchain radical formed by hydrogen abstraction in the methylene group has been observed in a small amount in the γ-radiolyses of PAA[22] and the methyl ester of PMAA.[21,25,26] the formation is believed to be a result of consecutive reactions. We have also found the midchain radical on the plasma-irradiation of the methyl esters of PMAA, but not on that of PMAA.[25] This seems to show that the formation of the midchain radical on the methylene group is not a direct irradiation effect.

The calculated potential curves for the bond cleavage of various bonds in TPA, DPA, acetic acid, and methyl acetate are shown in Figs. 1, 2, 3, and 4. It is difficult to specify the excited state responsible for the reactions, since the γ- and plasma-irradiation experiments are not selective for the excited states. The small differences in energy among the excited states given in Table 2 and in Figs. 1 and 2 may cause internal conversion from the higher excited states to the lowest excited state with high efficiency. Also, in the potential curves of the α-C–H bond cleavage of DPA in Fig. 2b the energy barrier in the lowest excited singlet state is apparently lower than those in the higher excited states, although there is no distinct difference in the energy barrier among the potential curves in the higher excited states. The experimentally known facility in the α-C–H bond cleavage of PAA is well reproduced by the features of the potential curves in the lowest excited singlet state of DPA. From these results, it is considered that the lowest excited states are closely related to the reactions of PAA and PMAA upon γ- and plasma-irradiation. The energy barriers of bond cleavages in the lowest excited singlet are summarized in Table 3, together with those in the lowest triplet states.

From the results, the main chain cleavage is apparently not the major reaction pathway in the excited states for both TPA and DPA. The most feasible bond cleavage in the excited state of TPA is decarboxylation in both the singlet and triplet states, as shown by the potential curves in Fig. 1, and by the energy barriers in Table 3. On the other hand, that of DPA is cleavage of the α-C–H bond in the excited singlet state, and cleavage of the α-C–H bond and decarboxylation in the triplet state.

Thus, the energy barriers of bond cleavages in the calculated potential curve of the lowest excited singlet state seem to well correspond to the experimentally known results, although we cannot ignore the contribution of the triplet state in view of a generally accepted high probability of intersystem crossing in car-

Table 1. Singlet–Singlet Transition Energies and Oscillator Strengths of Acetic Acid

Calculated				Observed[a]	
Energy eV	Wave length Å	Oscillator strength	Assign.	Wave length Å	Assign.
5.953	2083	0.0012	$n\rightarrow\pi^*$	2150(2000–2500)	$n\rightarrow\pi^*$
6.782	1828	0.0939	$n\rightarrow\sigma^*$	1724(1667–1900)	$n\rightarrow\pi^*$
8.019	1546	0.0013	$\pi\rightarrow\pi^*$	1587(1538–1667)	$n\rightarrow\sigma^*$
8.225	1507	0.0035	$n\rightarrow\sigma^*$	1500(1389–1538)	$\pi\rightarrow\pi^*$
8.652	1433	0.0026	$n'\rightarrow\pi^*$		
8.701	1425	0.0048	$n\rightarrow\sigma^*$		
8.821	1406	0.0041	$\pi\rightarrow\sigma^*$		
9.132	1358	0.0917	$\pi\rightarrow\pi^*$, $n\rightarrow\sigma^*$		
9.231	1343	0.1275	$n'\rightarrow\sigma^*$	1350(1250–1389)	$n\rightarrow\sigma^*$, $n\rightarrow R$
9.688	1280	0.0715	$n\rightarrow\sigma^*$		

a) Ref. 35

Table 2. Calculated Singlet–Singlet Transition Energies and Oscillator Strengths of TPA and DPA

TPA			DPA		
Energy eV	Wave length Å	Oscillator strength	Energy eV	Wave length Å	Oscillator strength
6.367	1947	0.0191	6.294	1970	0.0204
6.391	1940	0.0065	6.327	1960	0.0019
6.601	1878	0.1280	6.726	1843	0.2191
6.607	1877	0.2300	6.745	1838	0.1807
7.443	1666	0.0209	7.520	1649	0.0232
7.515	1650	0.0483	7.712	1608	0.0126
7.580	1636	0.3816	7.803	1589	0.0423
7.671	1616	0.0200	7.872	1575	0.0183
7.683	1614	0.1841	7.998	1550	0.2648
7.762	1597	0.0070	8.185	1515	0.0333

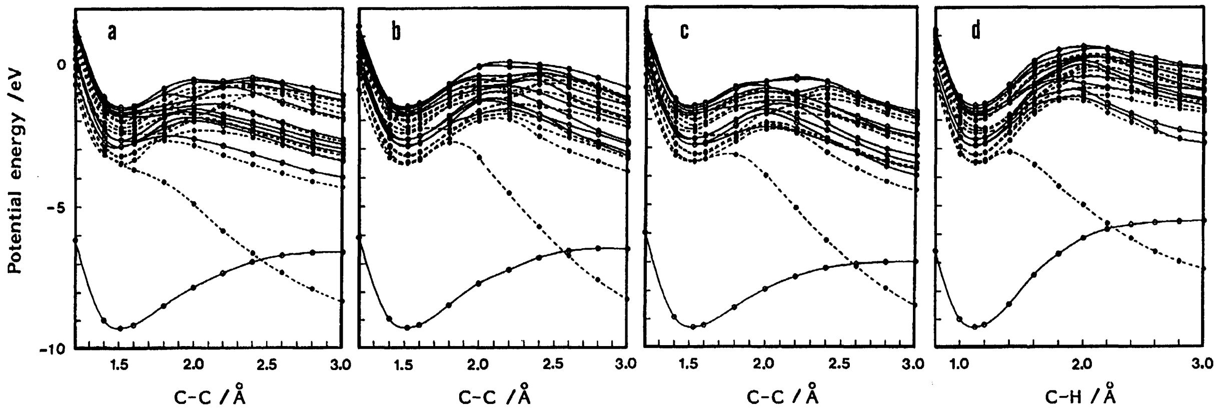


Fig. 1. Potential curves in the bond cleavage of TPA: (a) decarboxylation (b) C–CH_3 cleavage, (c) main-chain C–C cleavage, (d) methylene C–H cleavage, (——●——) singlet, (---●---) triplet.

bonyl compounds. Also, the difference in the nature of the bond cleavage in the lowest excited singlet state between TPA and DPA well corresponds to the experimental results for the vacuum ultraviolet (VUV) photolysis of small carboxylic acids.41) That is, it has been reported that the major radicals formed by the photolysis of primary and secondary alkanecarboxylic acids are those formed by α-C–H bond cleavage, and that the photolysis of tertiary carboxylic acid gives only the decarboxylated radical.41)

Thus, the formation of free radicals in the radiolysis of PMAA, PAA, and their esters was well explained based on the photoexcited states of the nonionic species.

In this study we ignored the Rydberg transitions, which have been known to have a large contribution to the excitation of carboxylic acids with an energy greater

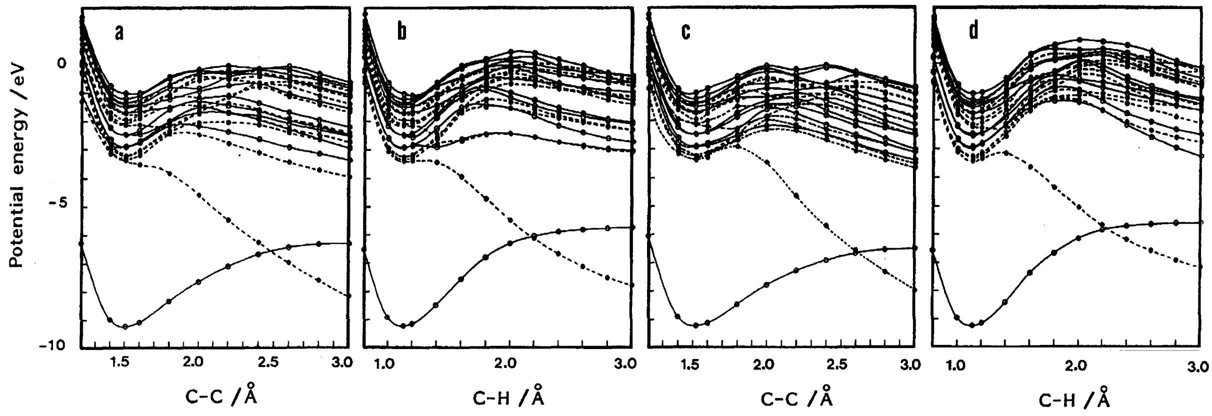


Fig. 2. Potential curves in the bond cleavage of DPA: (a) decarboxylation, (b) α-C–H cleavage, (c) main-chain C–C cleavage, (d) methylene C–H cleavage, (——●——) singlet, (- - -●- - -) triplet.

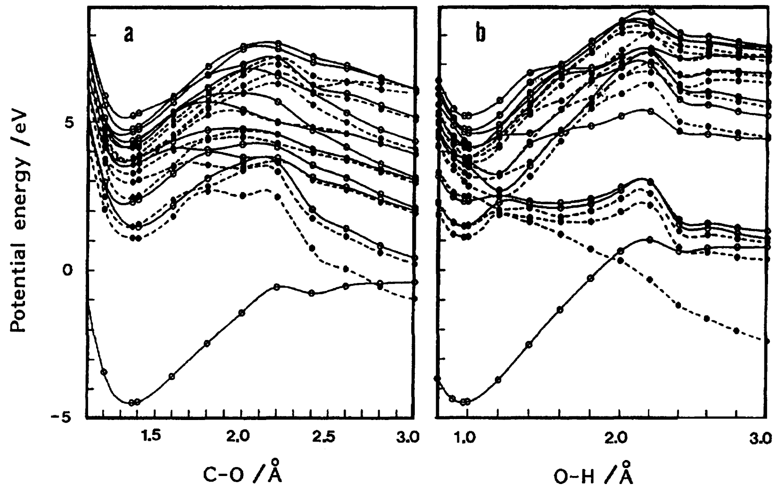


Fig. 3. Potential curves in the bond cleavage of acetic acid: (a) C–OH cleavage, (b) O–H cleavage, (——●——) singlet, (- - -●- - -) triplet.

than 8 eV.[35] Rydberg states are similar in the electronic state to the ground states of the cation radical. The ionized species has been reported in studies of γ-irradiated PAA and PMAA at low temperature;[23,24] also, decarboxylations in the cation radicals are well known as important fragmentation in the mass spectra of carboxylic acids. Thus, the possibility of reactions from the Rydberg states and in the ionized species cannot be ruled out based on the results of this study.

β-Cleavage in Radicals Formed by Side-Chain Cleavage. The major radicals observed in the γ- and plasma-irradiation of PMAA and its esters are the terminating radicals formed by β-cleavage following decarboxylation.[21—23,25,26] β-Cleavage in PMAA and its esters is considered to be quite a feasible pathway, since the radicals formed by decarboxylation have never been reported. On the other hand, the radicals formed by α-C–H bond cleavage in PAA and its esters have been reported,[21,23] and appears to be rather stable compared to the radical formed by decarboxylation in PMAA and its esters. However, there is still no consistent opinion concerning the characteristics of the radiolysis of PAA, due to the uncertainty of the ESR spectral assignments.

The reaction potentials of β-cleavage in the radicals formed by the above-mentioned side scissions in PMAA and PAA were calculated for model radical structures derived from TPA and DPA. The results are shown in Figs. 5 and 6.

In the calculated potential curves, β-C–H bond cleavages are apparently not feasible for both PMMA and PAA. Also, β-C–C cleavages in the ground and lowest excited states seem not to be as feasible as expected based on the experimental results. The feasibility of β-C–C cleavage could be substantiated by the nearly flat potential curves in the higher excited states. The transition energies in the radicals are considerably lower than those in TPA and DPA, as shown in Table 4. Transitions to the higher excited states may therefore occur easily.

Although the difference in the reaction potential of the β-C–C cleavage between PMAA and PAA is quite small, the increase in the potential energy accompany-

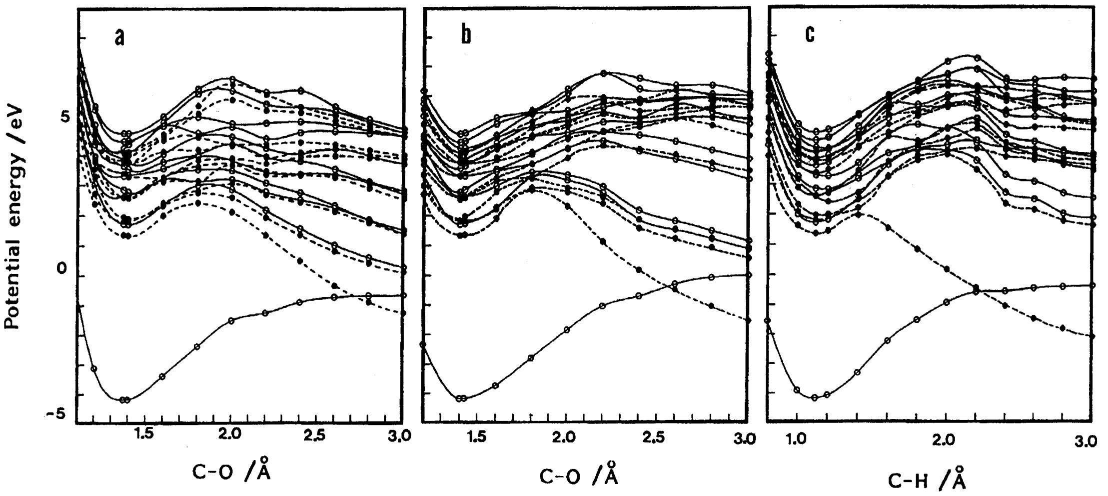


Fig. 4. Potential curves in the bond cleavage of methyl acetate: (a) C–OCH_3 cleavage, (b) O–CH_3 cleavage, (c) H–CH_2O cleavage, (—●—) singlet, (- - -●- - -) triplet.

Table 3. Energy Barriers (kcal mol^{-1}) in Calculated Potential Curves of Bond Cleavages

Compound	Type of bond cleavage	Ground state	Lowest excited singlet state	Lowest triplet state
TPA	C∼COOH	62	9	0
	H_3C∼C–COOH	64	30	16
	C∼C (main chain)	53	15	6
	C∼H (–CH_2–)	86	38	9
DPA	C∼COOH	67	17	0
	H∼C–COOH	81	9	0
	C∼C (main chain)	63	17	11
	C∼H (–CH_2–)	84	38	6
CH_3COOH	H_3C∼COOH	78	44	9
	O=C∼OH	95	53	37
	O=C–O∼H	126	35	18
CH_3COOCH_3	O=C∼OCH_3	81	30	25
	O=C–O∼CH_3	96	37	34
	C∼H (OCH_3)	88	56	14

1 cal=4.184 J.

ing progress of the reaction in the higher excited states of PAA is greater than that of PMAA. This might be the essential reason for the lower reactivity of the β-C–C cleavage in PAA than in PMAA.

Conclusion

The natures of the photocleavages of PMAA and PAA were investigated based on the reaction potentials of the model molecules calculated by molecular-orbital methods. The reaction potentials of the lowest excited states showed that among a variety of the bond cleavages the most feasible one is decarboxylation in PMAA and α-C–H bond cleavage in PAA. The calculated results were in good agreement with the experimental results for the radiolysis of the polymers, including the plasmolysis, and for the VUV photolysis of small carboxylic acids.

Also, the calculated reaction potentials of β-cleavages in radicals formed by the above-mentioned side-bond cleavages showed that β-C–C bond cleavages of the main chain are apparently more feasible than β-C–H bond cleavages of the methylene group. The feasibility of a β-cleavage in a radical of PMAA was attributed to the flat nature of the reaction potentials in the higher excited states.

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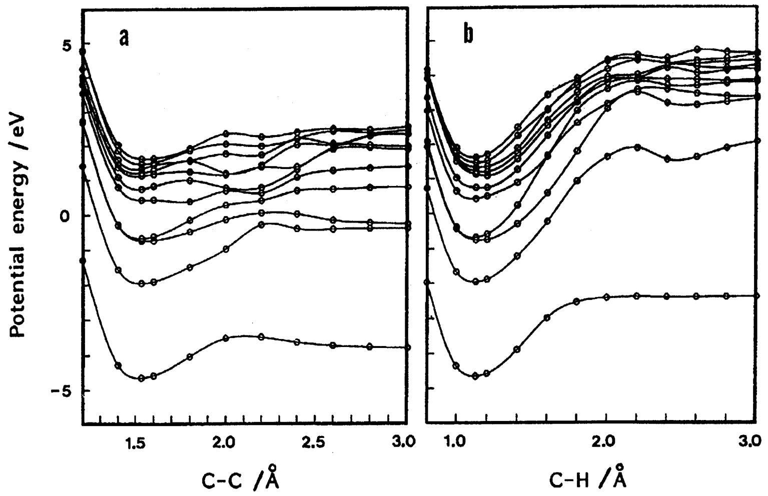

Fig. 5. Potential curves in the β-cleavage of the decarboxylated TPA radical: (a) C–C cleavage, (b) C–H cleavage.

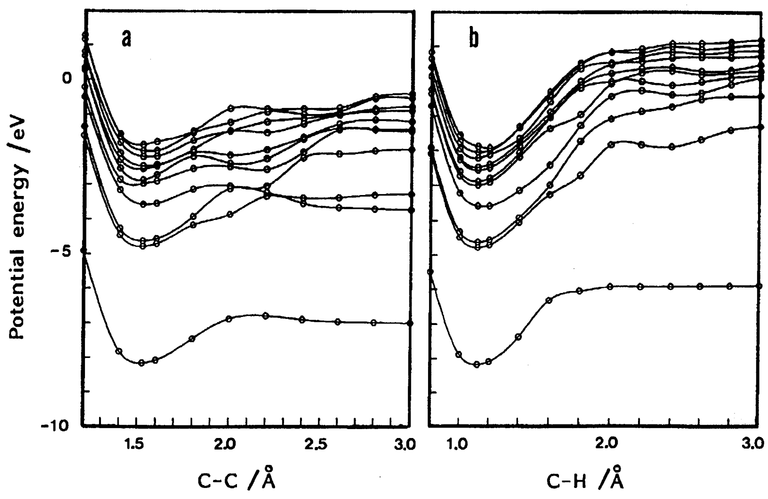

Fig. 6. Potential curves in the β-cleavage of the α-hydrogen abstracted DPA radical: (a) C–C cleavage, (b) C–H cleavage.

Table 4. Calculated Doublet–Doublet Transition Energies and Oscillator Strengths of Radicals Formed by Side-Chain Scissions in TPA and DPA

TPA-COOH			DPA-H		
Energy eV	Wave length Å	Oscillator strength	Energy eV	Wave length Å	Oscillator strength
2.692	4606	0.0143	3.378	3671	0.0016
3.898	3180	0.0017	3.537	3505	0.0109
3.971	3122	0.0008	4.583	2705	0.0003
5.070	2446	0.0149	5.173	2397	0.0032
5.387	2302	0.0217	5.285	2346	0.0149
5.775	2147	0.0256	5.602	2213	0.0108
5.860	2116	0.0290	5.687	2180	0.0113
5.978	2074	0.0018	5.953	2083	0.0983
6.116	2027	0.0105	6.119	2026	0.0313
6.266	1979	0.0127	6.289	1972	0.0599

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