

List of Papers and their Abstracts

Article No. 1:

Authors: El-Agamey, A.; McGarvey, D. J.,

Title: Acyl/aroxyperoxyl radicals: a comparative study of the reactivity of peroxy radicals resulting from the α -cleavage of ketones.

Journal Name: *Phys. Chem. Chem. Phys.*

Year, Vol., Page No.: 2002, 4(9), 1611-1617.

Abstract: Employing 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS^{2-}) as a selective radical probe, nanosecond laser flash photolysis (LFP) and competitive kinetic methods have been used to investigate the reactions of acyl/aroxyperoxyl radicals derived from the addition of oxygen to the α -cleavage products of various ketones in methanol. The selectivity of ABTS^{2-} for acyl/aroxyperoxyl radicals (as opposed to alkylperoxyl radicals), under the experimental conditions used, is supported by the oxygen concentration dependence of the $\text{ABTS}^{\cdot-}$ radical ion absorption amplitudes for acyl radicals that undergo decarbonylation on sub-microsecond timescales. The oxygen concentration dependence of the $\text{ABTS}^{\cdot-}$ transient absorption reflects the competition between decarbonylation and oxygen addition and therefore this data also provides information on decarbonylation and oxygen addition rates. Further evidence in support of the selectivity of ABTS^{2-} for acyl/aroxyperoxyl radicals is the agreement between results obtained from using different ketone precursors for specific acyl/aroxyperoxyl radicals. The order of reactivity of the peroxy radicals towards ABTS^{2-} is found to be aroxyperoxyl > acylperoxyl >> alkylperoxyl. The use of ABTS^{2-} as a monitor for acyl/ aroxyperoxyl radicals has been exploited by using competitive kinetics to obtain rate constants for the reactions of various acyl/aroxyperoxyl radicals with vitamin E and trolox.

Article No. 2:

Authors: El-Agamey, A.; McGarvey, D. J.,

Title: Carotenoid addition radicals do not react with molecular oxygen:
Aspects of carotenoid reactions with acylperoxyl radicals in polar and non-polar media.

Journal Name: *Free Rad. Res.*,

Year, Vol., Page No.: 2002, 36, 97-100 (Suppl. S).

Article No. 3:**Authors:** El-Agamey, A.; McGarvey, D. J.,**Title:** Evidence for a lack of reactivity of carotenoid addition radicals towards oxygen: A laser flash photolysis study of the reactions of carotenoids with acylperoxyl radicals in polar and non-polar solvents,**Journal Name:** *J. Am. Chem. Soc.*,**Year, Vol., Page No.:** 2003, 125(11), 3330-3340.

Abstract: In this paper, we report the results of a laser flash photolysis study of the reactions of a range of carotenoids with acylperoxyl radicals in polar and nonpolar solvents. The results show, for the first time, that carotenoid addition radicals do not react with oxygen to form carotenoid peroxy radicals; an observation which is of significance in relation to antioxidant/pro-oxidant properties of carotenoids. Acylperoxyl radicals, generated by photolysis of ketone precursors in oxygenated solvents, display high reactivity toward carotenoids in both polar and nonpolar solvents, but the nature of the carotenoid radicals formed is dependent on solvent polarity. In hexane, acylperoxyl radicals react with carotenoids with rate constants in the region of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ and give rise to transient absorption changes in the visible region that are attributed to the formation of addition radicals. All of the carotenoids show bleaching in the region of ground-state absorption and, with the exception of 7,7'-dihydro- β -carotene (77DH), no distinct absorption features due to addition radicals are observed beyond the ground state absorption region. For 77DH, the addition radical displays an absorption band that is spectrally resolved from the parent carotenoid absorption. The rate of decay of the 77DH addition radical is unaffected by oxygen in the concentration range 10^{-4} - 10^{-2} M, suggesting that these resonance-stabilized carbon-centered radicals are not scavenged by oxygen. At low incident laser intensities, the 77DH addition radical decay kinetics are 1st order with $k_1 \approx 4 \times 10^3 \text{ s}^{-1}$ at room temperature. The 1st order decay is attributed to an intramolecular cyclization process, which is supported by the substantial negative entropies of activation obtained from measurements of the decay rate constants for different 77DH addition radicals as a function of temperature. No transient absorption features are observed in the red or near-infrared regions in hexane for any of the carotenoids studied. In polar solvents such as methanol, acylperoxyl radicals also react with carotenoids with rate constants in the region of $10^9 \text{ M}^{-1} \text{ s}^{-1}$, but give rise to transient absorption changes in both the visible and the red/near-infrared regions, where it is evident that there are two distinct species. For 77DH, the addition radical absorption around 450 nm is still evident, although its kinetic behavior differs from its behavior in hexane. For 77DH and ζ -carotene (ζ -CAR) the spectral and kinetic resolution of the various absorption bands simplifies kinetic analysis. The kinetic evidence suggests that addition radical formation precedes formation of the two near-infrared absorbing species, and that the

kinetics of the addition radical decay match the kinetics of formation of the first of these species (NIR1, absorbing at shorter wavelengths). The decay of NIR1 leads to NIR2, which is attributed to the carotenoid radical cation. The solvent dielectric constant dependence of the relative amounts of NIR1 and NIR2 formed leads us to speculate that NIR1 is an ion-pair. However, an alternative assignment for NIR1 is an isomer of the radical cation. The results, in terms of the pattern of reactivity the carotenoids display and of the properties of the carotenoid radicals formed, are discussed in relation to the antioxidant/pro-oxidant properties of carotenoids.

Article No. 4:

Authors: El-Agamey, A.; Lowe, G. M.; McGarvey, D. J.; Mortensen, A.; Phillip, D. M.; Truscott, T. G.; Young, A. J.,

Title: Carotenoid radical chemistry and antioxidant/pro-oxidant properties,

Journal Name: *Arch. Biochem. Biophys.*,

Year, Vol., Page No.: 2004, 430(1), 37-48.

Abstract: The purpose of this review is to summarise the current state of knowledge of (i) the kinetics and mechanisms of radical reactions with carotenoids, (ii) the properties of carotenoid radicals, and (iii) the antioxidant/pro-oxidant properties of carotenoids.

Article No. 5:

Authors: El-Agamey, A.; Cantrell, A.; Land, E. J.; McGarvey, D. J.; Truscott, T. G.,

Title: Are dietary carotenoids beneficial? Reactions of carotenoids with oxy-radicals and singlet oxygen,

Journal Name: *Photochem. Photobiol. Sci.*,

Year, Vol., Page No.: 2004, 3(8), 802-811.

Abstract: Carotenoids play diverse roles in biology and medicine. Both the quenching of singlet oxygen (energy transfer) and interaction with oxy-radicals (electron transfer, H-atom transfer and addition reactions) are key processes in understanding many of these roles. Much previous work in 'simple' solvents is reviewed and new results in cell membrane models are presented. The possible consequences of using carotenoids as dietary supplements are discussed.

Article No. 6:

Authors: El-Agamey, A.; Burke, M.; Edge, R.; Land, E. J.; McGarvey, D. J.;

Truscott, T. G.,

Title: Photolysis of carotenoids in chloroform: enhanced yields of carotenoid radical cations in the presence of a tryptophan ester,

Journal Name: *Radiat. Phys. Chem.*,

Year, Vol., Page No.: 2005, 72(2-3), 341-345.

Abstract: The presence of an acetyl tryptophan ester gives rise to enhanced yields of carotenoid radical cations in chloroform following 355 nm laser excitation of the carotenoid, even though the tryptophan does not absorb at this wavelength. The increase is attributed to positive charge transfer from semi-oxidized tryptophan itself generated by light absorbed by the carotenoid. The mechanism of these radical processes has been elucidated by pulse radiolysis studies.

Article No. 7:

Authors: El-Agamey, A.; McGarvey, D. J.,

Title: First direct observation of reversible oxygen addition to a carotenoid-derived carbon-centered neutral radical,

Journal Name: *Org. Lett.*,

Year, Vol., Page No.: 2005, 7(18), 3957-3960.

Abstract: Direct observation of reversible oxygen addition to a carotenoid-derived carbon-centered neutral radical is reported for the first time. The influence of temperature on the observed reaction kinetics has been used to obtain kinetic and thermodynamic parameters relating to the reversible addition of oxygen to the carotenoid radical obtained from reaction of 7,7'-dihydro- β -carotene (77DH) with phenylthiyl radical (PhS \cdot) in benzene. In addition, the rate constant for oxygen addition to the equivalent β -carotene (β -CAR) derived radical is also reported.

Article No. 8:

Authors: Enes, R. F.; Tomé, A. C.; Cavaleiro, J. A. S.; El-Agamey, A.;

McGarvey, D. J.,

Title: Synthesis and solvent dependence of the photophysical properties of [60]fullerene–sugar conjugates,

Journal Name: *Tetrahedron*,

Year, Vol., Page No.: 2005, 61 (50), 11873-11881.

Abstract: A method for the synthesis of optically pure C60 derivatives containing one or two D-galactose or D-glucose units is described. It involves the synthesis of sugar–malonate derivatives followed by a cyclopropanation reaction with C60. The solvent dependence of the photophysical properties of the methano[60]fullerene–sugar derivatives was studied using nanosecond laser flash photolysis coupled with kinetic UV–vis absorption spectroscopy and time-resolved singlet oxygen luminescence measurements. The triplet properties of these fullerenes, including transient absorption spectra, molar absorption coefficients and quantum yield for the photosensitised production of $^1\text{O}_2$ were determined in toluene, benzonitrile and acetonitrile solutions. The transient absorption spectral profiles are solvent independent although small differences are observed in the transient absorption maximum: 720 ± 5 nm for toluene, 710 ± 5 nm for benzonitrile and 700 ± 5 nm for acetonitrile. Triplet state molar absorption coefficients (ϵ_T) of C60 derivatives vary from 9456 ± 2090 M^{-1} cm^{-1} , for compound 10 in toluene, and $15,272\pm 4462$ M^{-1} cm^{-1} , for compound 6 in acetonitrile. Triplet state lifetimes (τ_T) for methano[60]fullerene–sugar derivatives, under our experimental conditions, are similar in toluene or benzonitrile solutions (47.5 ± 1.1 $\mu\text{s} \leq \tau_T \leq 51.4\pm 2.0$ μs) but are lower in acetonitrile solutions (31.8 ± 0.6 $\mu\text{s} \leq \tau_T \leq 43.0\pm 1.1$ μs). Toluene and benzonitrile solutions of C60 derivatives have $\phi\Delta$ close to unity.

Article No. 9:

Authors: El-Agamey, A.; Edge, R.; Navaratnam, S.; Land, E. J.; Truscott, T.

G.,

Title: Carotenoid radical anions and their protonated derivatives,

Journal Name: *Org. Lett.*,

Year, Vol., Page No.: 2006, 8 (19), 4255-4258.

Abstract: In this study, we report the protonation reactions for astaxanthin and canthaxanthin radical anions in methanol, alkaline methanol, and aqueous 2% Triton X-100 at different pH values. The pK_a values for the corresponding α -hydroxy radical derivatives of astaxanthin, canthaxanthin, and β -*apo-8'-carotenal* were estimated in 2% Triton X-100. Also, the effects of the microenvironment and the structure of the carotenoids on the protonation rate constant are discussed.

Article No. 10:

Authors: El-Agamey, A.; McGarvey, D. J.,

Title: The reactivity of carotenoid radicals with oxygen,

Journal Name: *Free Rad. Res.*,

Year, Vol., Page No.: 2007, 41(3), 295-302.

Abstract: The possibility that carotenoid radicals react with oxygen to form chain-carrying peroxy radicals has been postulated to account for the reduction in antioxidant effectiveness displayed by some carotenoids at high oxygen concentrations. The primary objective of the work described in this paper was to measure the rate constants for oxygen addition to a series of carotenoid radicals and to examine any influence of carotenoid structural features on these rate constants. Laser flash photolysis has been used to generate long-lived carotenoid radicals (PhS-CAR[•]) derived from radical addition reactions with phenylthiyl radicals (PhS[•]) in benzene. The PhS-CAR[•] radicals are scavenged by oxygen at rates that display a moderate dependence on the number of conjugated double bonds (ndb) in the carotenoid. The rate constants range from $\sim 10^3$ to $\sim 10^4$ M⁻¹ s⁻¹ for ndb = 7–11. The data also suggest that the presence of terminal cyclic groups may cause an increase in the rate constant for oxygen addition.

Article No. 11:

Authors: Edge, R.; El-Agamey, A.; Land, E. J.; Navaratnam, S.; Truscott, T.

G.,

Title: Studies of carotenoid one-electron reduction radicals,

Journal Name: *Arch. Biochem. Biophys.*,

Year, Vol., Page No.: 2007, 458, 104-110.

Abstract: The relative reduction potentials of a variety of carotenoids have been established by monitoring the reaction of carotenoid radical anion ($CAR1^{\cdot-}$) with another carotenoid ($CAR2$) in hexane and benzene. This order is consistent with the reactivities of the carotenoid radical anions with porphyrins and oxygen in hexane. In addition, investigation of the reactions of carotenoids with reducing radicals in aqueous 2% Triton-X 100, such as carbon dioxide radical anion ($CO_2^{\cdot-}$), acetone ketyl radical ($AC^{\cdot-}$) and the corresponding neutral 2 radical (ACH^{\cdot}), reveals that the reduction potentials for β -carotene and zeaxanthin lie in the range 1950 to 2100 mV and those for astaxanthin, canthaxanthin and β -apo-80-carotenal are more positive than 1450 mV. This illustrates that the presence of a carbonyl group causes the reducing ability to decrease. The radical cations have been previously shown to be strong oxidising agents and we now show that the radical anions are very strong reducing agents.

Article No. 12:

Authors: El-Agamey, A.; McGarvey, D. J.,

Editors: in: Britton, G.; Liaaen-Jensen, S.; Pfander, H. (Eds.),

Book Title: Carotenoids Volume 4: Natural Functions,

Chapter Title: Carotenoid Radicals and Radical Ions

Year, Page No.: 2008, 119-154.

Publisher: Birkhäuser, Basel,

Article No. 13:

Authors: El-Agamey, A.,

Title: Laser flash photolysis of new water-soluble peroxy radical precursor,

Journal Name: *J. Photochem. Photobiol. A: Chem.*,

Year, Vol., Page No.: 2009, 203, 13-17.

Abstract: Laser flash photolysis (LFP) of commercially available water-soluble 4-acetyl-4-phenylpiperidine hydrochloride (APP) in the presence of oxygen gives rise to acetylperoxy radical (ACP). The formation of ACP during LFP of APP has been established by determining their rate constants with ABTS^{2-} in methanolic and aqueous solutions (0.15 ± 0.02 and $2.0 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively). These rate constants are in agreement with those reported in the literature.

The reactivity of ACP was investigated with crocin in aqueous and methanolic solutions. Moreover, the rate constant for the reaction of ACP with nitrite anion (NO_2^-) in aqueous solution was determined to be $4.45 \pm 0.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Overall, APP can be used as ACP precursor in aqueous and organic solutions using the more accessible LFP technique than the normally used (especially in aqueous solutions) pulse radiolysis technique.

Article No. 14:

Authors: El-Agamey, A.; Fukuzumi, S.; Naqvi, K. R.; McGarvey, D. J.,

Title: Kinetic studies of retinol addition radicals,

Journal Name: *Org. Biomol. Chem.*,

Year, Vol., Page No.: 2011, 9, 1459-1465.

Abstract: Retinol neutral radicals (RS-retinol[•]), generated from the reaction of retinol with 4-pyridylthiyl and 2-pyridylthiyl radicals in argon-saturated methanol, undergo β-elimination, which can be monitored *via* the slow secondary absorption rise at 380 nm attributed to the rearrangement of the unstable retinol neutral addition radicals to the more stable addition radicals. Rate constants for the β-elimination reactions (k_{β}) of 4-PyrS-retinol[•] were measured at different temperatures and the Arrhenius equation for the reaction is described by $\log(k_{\beta}/s^{-1}) = (12.7 \pm 0.2) - (54.3 \pm 1.3)/\theta$, where $\theta = 2.3RT \text{ kJ mol}^{-1}$. The reactivities of retinol addition radicals (RS-retinol[•]), generated from the reaction of retinol with various thiyl radicals, towards oxygen have also been investigated in methanol. In the presence of oxygen, the decay of RS-retinol[•] fits to biexponential kinetics and both observed rate constants for the RS-retinol[•] decay are oxygen-concentration dependent. This suggests that at least two thiyl addition radicals, formed from the reaction of RS[•] with retinol, undergo oxygen addition reactions. In light of the estimated rate constants for oxygen addition to RS-retinol[•] and RS-CAR[•] (CAR: carotenoid), the antioxidant-prooxidant properties of retinol are discussed.

Article No. 15:**Authors:** El-Agamey, A.; Fukuzumi, S.,**Title:** Laser flash photolysis study on the retinol radical cation in polar solvents,**Journal Name:** *Org. Biomol. Chem.*,**Year, Vol., Page No.:** 2011, 9, 6437-6446.

Abstract: Laser flash photolysis (LFP) of retinol in argon-saturated methanol gives rise to a transient at 580 nm (transient A). Formation of transient A is accompanied by a transient growth at 370 nm. The rate of this growth is retinol concentration-dependent. The transient growth at 370 nm was removed in the presence of N₂O, which is known to scavenge solvated electrons. These results can be interpreted by formation of retinol^{•+} ($\lambda_{\text{max}} = 580 \text{ nm}$) and solvated electrons following LFP of retinol. Subsequently, the solvated electrons are rapidly scavenged by retinol to form retinol⁻ ($\lambda_{\text{max}} = 370 \text{ nm}$ in methanol). On the other hand, transient A is not ascribed to the retinyl cation, as was previously proposed, because the retinyl cation, generated from LFP of retinyl acetate, and transient A show different reactivities towards halide ions (e.g. $k_{\text{Br}^-} = 1.7 \times 10^9$ and $1.51 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ respectively, in acetonitrile). After demonstrating the identity of transient A as retinol^{•+}, its reactions with carotenoids were examined in air-saturated polar solvents. In the presence of carotenoids, an enhancement in the decay of retinol^{•+} was observed and was accompanied by formation of the corresponding carotenoid radical cations *via* electron transfer from carotenoids to retinol^{•+}. Furthermore, the reactivity of retinol^{•+} towards pyridine derivatives was investigated in air-saturated polar solvents. It was found that the decay of retinol^{•+} was accelerated with concomitant formation, with the same rate, of a transient at 370 nm. Similar observations were obtained with increasing pH of air-saturated aqueous 2% Triton X-100 of retinol^{•+}. The 370 nm (or 380 nm in the case of Triton X-100) transient is attributed to the base adducts or deprotonated neutral radicals. On the basis of these results, the activities of the retinyl cation and retinol^{•+} are compared and the consequences of retinol^{•+} formation within biological environments are discussed.

Article No. 16:**Authors:** El-Agamey, A.; Fukuzumi, S.,**Title:** The Remarkable Effect of the Manganese Ion with Dioxygen on the Stability of π -Conjugated Radical Cations,**Journal Name:** *Chem. Eur. J.*,**Year, Vol., Page No.:** 2012, 18, 14660 – 14670.

Abstract: In this paper, nanosecond laser flash photolysis has been used to investigate the influence of metal ions on the kinetics of radical cations of a range of carotenoids (astaxanthin (ASTA), canthaxanthin (CAN), and β -carotene (β -CAR)) and various electron donors (1,4-diphenyl-1,3-butadiene (14DPB), 1,6-diphenyl-1,3,5-hexatriene (16DPH), 4-methoxy-trans-stilbene (4 MeOSt), and trans-stilbene (trans-St)) in benzonitrile. Radical cations have been generated by means of photosensitized electron-transfer (ET) using 1,4-dicyanonaphthalene (14DCN) and biphenyl (BP). The kinetic decay of CAR^{*+} shows a strong dependence on the identity of the examined metal ion. For example, whereas $NaClO_4$ has a weak effect on the kinetics of CAR^{*+} , $Ni(ClO_4)_2$ causes a strong retardation of the decay of CAR^{*+} . It is also interesting to note that Mn^{2+} , which is a biologically relevant metal ion, shows the strongest effect of all the investigated metal ions (e.g., in the presence of Mn^{2+} ions, the half-life ($t_{1/2}$) of CAN^{*+} ($t_{1/2} > 90$ ms) is more than three orders of magnitude higher than in the absence of the metal ions ($t_{1/2} \sim 16$ μ s)). Furthermore, the influence of metal-ion and oxygen concentrations on the kinetics of CAR^{*+} reveals their pronounced effect on the kinetic decay of CAR^{*+} . However, these remarkable effects are greatly diminished if either oxygen or metal ions are removed from the investigated solutions. Therefore, it can be concluded that oxygen and metal ions interact cooperatively to induce the observed substantial effects on the stabilities of CAR^{*+} . These results are the first direct observation of the major role of oxygen in the stabilization of radical cations, and they support the earlier mechanism proposed by Astruc et al. for the role of oxygen in the inhibition of cage reactions. On the basis of these results, the factors that affect the stability of radical cations are discussed and the mechanism that shows the role of oxygen and metal ions in the enhancement of radical-cation stability is described.

Article No. 17:

Authors: El-Agamey, A.; El-Hagrasy, M.; Tomoyoshi, S.; Fukuzumi, S.,

Title: Influence of pH on the decay of β -carotene radical cation in aqueous Triton X-100: A laser flash photolysis study,

Journal Name: *J. Photochem. Photobiol. B: Biol.*,

Year, Vol., Page No.: 2015, 146, 68-73.

Abstract: The identification of the spectral information of carotenoid neutral radicals is essential for studying their reactivities towards O_2 and thereby evaluating their role in the antioxidant–prooxidant properties of the corresponding carotenoid. Recently, it was reported that β -carotene neutral radical (β -CAR \cdot) has an absorption maximum at 750 nm. This contradicts the results of many reports that show carotenoid neutral radicals (CAR \cdot) absorb in the same or near to the spectral region as their parent carotenoids. In this manuscript, the influence of pH on the decay of β -carotene radical cation (β -CAR-H $^{+\cdot}$), generated in an aqueous solution of 2% Triton X-100 (TX-100), was investigated, employing laser flash photolysis (LFP) coupled with kinetic absorption spectroscopy, to identify the absorption bands of the β -carotene neutral radicals. By increasing the pH value of the solution, the decay of β -CAR-H $^{+\cdot}$ is enhanced and this enhancement is not associated with the formation of any positive absorption bands over the range 550–900 nm. By comparing these results with the literature, it can be concluded that β -carotene neutral radicals most probably absorb within the same spectral range as that of β -carotene. The reaction pathways of the reaction of β -CAR-H $^{+\cdot}$ with \cdot OH have been discussed.

Article No. 18:**Authors:** El-Agamey, A.; McGarvey, D. J.,**Title:** Peroxyl radical reactions with carotenoids in microemulsions: Influence of microemulsion composition and the nature of peroxyl radical precursor,**Journal Name:** *Free Rad. Biol. Med.*,**Year, Vol., Page No.:** 2016, 90, 75-84.

Abstract: The reactions of acetylperoxyl radicals with different carotenoids (7,7'-dihydro- β -carotene and ζ -carotene) in SDS and CTAC microemulsions of different compositions were investigated using laser flash photolysis (LFP) coupled with kinetic absorption spectroscopy. The primary objective of this study was to explore the influence of microemulsion composition and the type of surfactant used on the yields and kinetics of various transients formed from the reaction of acetylperoxyl radicals with carotenoids. Also, the influence of the site (hydrocarbon phases or aqueous phase) of generation of the peroxyl radical precursor was examined by using 4-acetyl-4-phenylpiperidine hydrochloride (APPHCl) and 1,1-diphenylacetone (11DPA) as water-soluble and lipid-soluble peroxyl radical precursors, respectively. LFP of peroxyl radical precursors with 7,7'-dihydro- β -carotene (77DH) in different microemulsions gives rise to the formation of three distinct transients namely addition radical ($\lambda_{\max} = 460$ nm), near infrared transient1 (NIR, $\lambda_{\max} = 700$ nm) and 7,7'-dihydro- β -carotene radical cation (77DH^{•+}, $\lambda_{\max} = 770$ nm). In addition, for ζ -carotene (ZETA) two transients (near infrared transient1 (NIR1, $\lambda_{\max} = 660$ nm) and ζ - carotene radical cation (ZETA^{•+}, $\lambda_{\max} = 730$ –740 nm)) are generated following LFP of peroxyl radical precursors in the presence of ζ -carotene (ZETA) in different microemulsions. The results show that the composition of the microemulsion strongly influences the observed yield and kinetics of the transients formed from the reactions of peroxyl radicals (acetylperoxyl radicals) with carotenoids (77DH and ZETA). Also, the type of surfactant used in the microemulsions influences the yield of the transients formed. The dependence of the transient yields and kinetics on microemulsion composition (or the type of surfactant used in the microemulsion) can be attributed to the change of the polarity of the microenvironment of the carotenoid. Furthermore, the nature of the peroxyl radical precursor used (water-soluble or lipid-soluble peroxyl radical precursors) has little influence on the yields and kinetics of the transients formed from the reaction of peroxyl radicals with carotenoids. In the context of the interest in carotenoids as radical scavenging antioxidants, the fates of the addition radicals (formed from the reaction of carotenoid with peroxyl radicals) and carotenoid radical cations are discussed.