in which there is reduced contact between **1** and the aqueous phase. In contrast, addition of 0.013 M methionine resulted in a photobleaching with no detectable isotope effect.

Taking into account these observations: a requirement for O_2, non-rate-determining attack of singlet oxygen and (in the case of methionine) the requirement of a thioether group that is a well-known substrate for singlet oxygen;[29] a mechanism involving attack on the porphyrin by an intermediate oxygenated species AO_2 (eq 2-5) can be proposed (where P = **1** or other porphyrin

$$P \rightarrow {}^1P^* \rightarrow {}^3P^* \quad (2)$$

$$^3P^* + O_2 \rightarrow P + {}^1O_2^* \quad (3)$$

$$^1O_2^* + A \rightarrow AO_2 \quad (4)$$

$$AO_2 + P \rightarrow AO + PO \rightarrow \text{other products} \quad (5)$$

and A is an amino acid or other primary acceptor). In the case of methionine, AO_2 is probably methionine persulfoxide ($R_1R_2S^+OO^-$) and methionine sulfoxide (AO) is detected as a product produced concomitantly with porphyrin photobleaching. Although primary porphyrin degradation products cannot be isolated under the reaction conditions, some clear structural inferences can be obtained. Thus while non-vinyl porphyrins such as mesoporphyrin IX and hematoporphyrin IX are relatively stable when irradiated in benzene or the microemulsion with oxygen, both porphyrins photodegrade rapidly in the microemulsions containing methionine. For all three porphyrins weak absorption near 650 and 360–370 nm grows in during prolonged irradiation. This absorption is characteristic of photolabile biliverdins.[14,30,31]

The rapid loss of absorption in the visible and near-UV is consistent with a reaction in which the porphyrin macrocycle itself is attacked followed by a ring opening to give linear pyrrole derivatives. It has been shown that certain metalloporphyrins are photooxygenated to yield formylbiliverdins as primary products;[31-34] however, in other cases where metal-free porphyrins are degraded in aqueous solution suspected formylbiliverdins cannot be isolated.[31] We suggest that the first product, PO, is probably an epoxide that subsequently converts to a formylbiliverdin hydrolytically. Biliverdins are well-known to degrade rapidly in the presence of singlet oxygen sensitizers.[35,36]

The intermediates, "AO_2", obtained with different amino acids or other membrane components should possess a variety of lifetimes and reactivities. We find, for example, in studies with methionine in the microemulsion, evidence for pronounced differences in reactivity between AO_2 and $^1O_2$. Thus while hematoporphyrin IX, mesoporphyrin IX, and the hydroxy aldehydes **2** and **3** are all relatively stable toward $^1O_2$, they are all rapidly degraded by AO_2 as evidenced by their accelerated bleaching by addition of methionine. In contrast the photobleaching of (tetraphenylporphyrin)zinc, which is rapidly converted to a biliverdin upon irradiation in homogeneous solution[31-34] or the microemulsion without methionine, is strongly quenched by addition of methionine to the microemulsion.

The most striking aspect of these studies to date is thus the finding that several amino acids can evidently generate relatively powerful oxidants subsequent to reaction with $^1O_2^*$. These ground-state reagents may be powerful agents in photodynamic action processes due to their relatively long lifetimes or localization at specific sites in in vivo systems. We are currently extending our studies to include a variety of natural membrane systems and other oxidizable "sensitizer substrates".

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Registry No. 1, 553-12-8; **2**, 70552-66-8; **3**, 89398-63-0; **4**, 89398-64-1; **5**, 10200-02-9; **6**, 60185-98-0; methionine, 63-68-3; histidine, 71-00-1; tryptophan, 73-22-3; oxygen, 7782-44-7.

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Autoxidation of Micelles and Model Membranes. Quantitative Kinetic Measurements Can Be Made by Using Either Water-Soluble or Lipid-Soluble Initiators with Water-Soluble or Lipid-Soluble Chain-Breaking Antioxidants[1]

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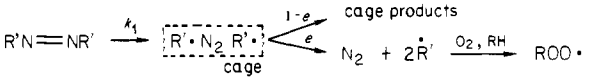
It is well-known that the autoxidation of biological membranes occurs readily and is associated with many important pathological events.[2] In 1980 quantitative kinetic studies of the autoxidation of phospholipid bilayers were first described in two preliminary communications,[3,4] one of which has since been fully amplified.[5] The difficulty that had to be overcome in these studies, as in all quantitative autoxidation kinetics, was that of ensuring that the initiation of the radical chain occurred at a reproducible and known rate. In both cases, this was achieved within the lipid bilayer by the thermal decomposition of a relatively large amount of a lipophilic azo compound.[3,4,6] Rates of initiation, R_i, were determined by the induction-period method[7] using lipophilic phenolic antioxidants (e.g., α-tocopherol, α-T[4]). The efficiencies of chain initiation, e, were also determined by measuring the rate of decomposition of the azo initiator.



$$R_i = 2ek_1[R'NNR']$$

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Table I. Autoxidation of Linoleic Acid (6.43×10^{-5} mol) in 2.0 mL of 0.5 M SDS Micelles in Water at 30 °C[a]

initiator,[b] (mol × 10^5)	inhibitor (mol × 10^8)	induction period × 10^{-3}, s	$10^9 R_i$,[c] M s^{-1}	e	$10^6 \times (-d[O_2]/dt)$,[d,e] M s^{-1}	oxidizability × 10^2,[d,e,f] $M^{-1/2}$ $s^{-1/2}$
DBHN (1.07)	α-T[g] (3.89)	3.92	9.9	0.29	3.40	4.7
(1.01)	(7.77)	8.21	9.5	0.29	3.33	4.7
(1.15)	TROLOX(−) (1.40)	1.48	9.5	0.26	2.57	3.7
(1.01)	(1.50)	1.48	10.1	0.31	2.73	3.7
(1.15)	(3.16)	2.99	10.6	0.29	3.55	4.8
ABAP (5.48)	α-T[g] (1.14)	2.88	4.0	0.57	1.46	3.2
(4.79)	(3.89)	15.1	2.6	0.43	2.03	5.5
(3.68)	TROLOX(−) (0.78)	2.95	2.6	0.56	1.25	3.4
(5.46)	(1.32)	3.89	3.4	0.49	1.46	3.5
(3.66)	(2.31)	9.47	2.4	0.53	1.25	3.5

[a] 0.1 M phosphate buffer, pH 7.0, containing 1×10^{-4} M ethylenediaminetetraacetic acid. Samples were prepared as described in ref 12. Chain lengths ($d[O_2]/dt \div R_i$ after correction for O_2 consumed by the initiator and adjustment to a common reaction volume) varied from 34 to 98. [b] [DBHN] measured by absorbance at 227 nm; k_i(DBHN) = 3.2×10^{-6} s^{-1}, k_i(ABAP) = 1.27×10^{-7} s^{-1}, both measured under these conditions. [c] Calculated for the 2.0-mL volume. [d] Based on volume of organic phase, see ref 14. [e] After induction period. [f] R_i has been converted to unit volume of organic phase, see ref 14. [g] [α-T] measured by absorbance at 292 nm.

Table II. Autoxidation of DLPC Multilamellar Liposomes (2.45×10^{-5} mol) in 2.0 mL of Water at 30 °C[a]

initiator[b] (mol × 10^5)	inhibitor (mol × 10^8)	induction period × 10^{-3}, s	$10^9 R_i$,[c] M s^{-1}	e	$10^6 \times (-d[O_2]/dt)$,[d,e] M s^{-1}	oxidizability × 10^2,[d,e,f] $M^{-1/2}$ $s^{-1/2}$
DBHN (1.14)	α-T[g] (5.01)	21.6	2.3	0.063	20.7	4.8
(0.91)	(2.53)	7.92	3.2	0.11	23.1	4.6
(1.03)	(2.66)	11.1	2.4	0.073	16.1	3.7
(1.03)	TROLOX(−) (2.87)	16.6	1.7	0.053	24.3	6.5
(0.82)	(2.03)	10.4	2.0	0.074	21.5	5.4
(0.96)	(1.47)	8.24	1.8	0.058	17.3	4.6
ABAP (3.67)	α-T[g] (3.51)	5.36	6.6	0.47	39.1	5.4
(3.70)	(1.25)	2.07	6.0	0.43	45.8	6.4
(3.69)	TROLOX(−) (1.50)	2.54	5.9	0.42	51.9	7.4
(3.65)	(3.14)	5.51	5.7	0.41	42.3	6.2

[a] 0.1 M phosphate buffer, pH 7.0, containing 1×10^{-4} M ethylenediaminetetraacetic acid. Liposomes were prepared as described in ref 5. α-T and DBHN, dissolved in CH_2Cl_2, were added to DLPC in CH_2Cl_2 prior to liposome formation. ABAP and TROLOX(−), in aqueous solution, were added after liposome formation during the course of the experiment. Chain lengths were 74–173 (see ref *a*, Table I). [b] [DBHN] measured by HPLC analysis; k_i(DBHN) = 3.2×10^{-6} s^{-1} (ref 5), k_i(ABAP) = 3.82×10^{-7} s^{-1}, both measured under these conditons. [c] Calculated for the 2.0-mL volume. [d] Based on volume of organic phase, see ref 14. [e] After induction period. [f] R_i has been converted to unit volume of organic phase, see ref 14. [g] [α-T] measured by HPLC analysis.

The possibility and potential importance for bilayer autoxidation of chemistry occurring at the aqueous–lipid interfacial region has been indicated by a number of suggestions and observations. For example, it was suggested earlier that peroxyl radicals formed in the nonpolar hydrocarbon interior of a bilayer may diffuse into and preferentially reside in this region[4,5,8] and that the chromanol portion of α-T, which is crucial for inhibition,[10] also resides here.[11] This should make it possible for water soluble molecules to interact *directly* with peroxyl radicals or α-T in the bilayer.

Our work on α-T/ascorbate interactions in the autoxidation of linoleic acid in sodium dodecyl sulfate, SDS, micelles[12,13] has led us to study the effect of using water soluble initiators and antioxidants. A few of our results are presented in Table I, the data for each run having been chosen to show the total range of values for e and for oxidizability[14] that were actually obtained; all other results fell within these limiting values. The lipid- and water-soluble initiators were di-*tert*-butylhyponitrite, DBHN, and azobis(2-amidinopropane hydrochloride) ABAP, respectively, and the lipid- and water-soluble inhibitors were α-T and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylate, TROLOX(−), respectively. Initiator efficiencies measured with α-T and with TROLOX(−) are identical for initiation by DBHN and by ABAP. Most importantly, the oxidizability of the linoleic acid[14] measured from R_i values and rates of autoxidation with both initiators are identical within experimental error.

Data given in Table II show that the oxidizabilities of multilamellar liposomes of dilinoleoylphosphatidylcholine, DLPC, are also the same within experimental error irrespective of whether this quantity is measured using water-soluble or lipid-solubile initiators and inhibitors.

The e values found for different initiators deserve comment. Thus, for DBHN e is considerably smaller in the multilamellar liposomes than in the SDS micelles and is smaller in the micelles than in chlorobenzene solution (e = 0.66).[5] These differences we attribute, as previously,[4,5] to the decrease in (micro)viscosity on going from bilayer, to micelle, to chlorobenzene. In contrast, for ABAP e has a similar magnitude in the liposome suspension as

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(14) Defined as $k_p/(2k_t)^{1/2}$ for the autoxidation of a substrate RH for which the uninhibited rate can be described by $-d[O_2]/dt = k_p[RH](R_i/2k_t)^{1/2}$, where k_p and $2k_t$ are the rate constants for chain propagation (ROO· + RH →) and termination (2R00· →), respectively, and [RH] is the concentration of oxidizable substrate in the organic phase. Volumes of organic phases were calculated on the following basis: micelles, 0.25 L/mol SDS;[12] phosphatidylcholine bilayers, density = 0.8.[5]

in the micellar system.[15] This is readily explained by assuming that the ABAP decomposes in the aqueous phase, as would be expected. More difficult to explain is the observation that ABAP decomposes 3 times less rapidly in 0.5 M SDS than in the liposome suspension, in water itself, in 0.1 M phosphate buffer (pH 7.0), or in 0.5 M sodium chloride/0.1 M phosphate buffer (pH 7.0).

Our present results show that *quantitative kinetic measurements on the autoxidation of heterogeneous systems are much less difficult than heretofore assumed.* It is interesting that in the liposomes, the charged, water-soluble initiator, ABAP, and inhibitor, TROLOX(-), though added after liposome formation, each appear to have had access to all layers of the multilamellar assembly. Our results also raise two intriguing possibilitites: first, that water soluble, chain-breaking antioxidants (either phenols or functionally related materials) may be present in vivo to supplement (lipid soluble) vitamin E; second, water soluble, chain-breaking antioxidants may have therapeutic value in the treatment of medical conditions (e.g., inflammation) suspected to involve lipid peroxidation.

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Registry No. Linoleic acid, 60-33-3; DLPC, 6542-05-8; DBHN, 14976-54-6; ABAP, 17688-97-0; α-T, 59-02-9; TROLOX(-), 89363-90-6.

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Macrocyclic Tridithiocarbamate as a Specific Uranophile

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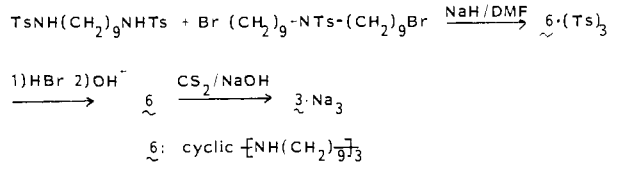
Molecular design for host molecules specific to certain guests is one of the most important and valuable concepts developed recently.[1-4] However, host-guest binding is extremely sensitive to local environment depending on the interaction mode and well-known alkaline metal ion binding capacity of crown ethers, for example, is diminished in its magnitude remarkably in an aqueous solution. Apparently, design for host molecules showing strong binding toward certain metal ions in water requires considerably stronger host-guest coordination interaction than guest-water (or OH^-) interaction. This requirement is fulfilled when negatively charged macrocycles of appropriate sizes are prepared.[5,6] As a typical and illustrative example, we have made molecular design for hosts specific to uranyl, UO_2^{2+}, showing that appropriately designed "uranophiles" **1**[5] and **2**[6] bound UO_2 very strongly.

In addition to large association equilibrium constants, "uranophiles" must show large association rate constants to avoid such a competing side reaction as rapid formation of polynuclear complexes leading to precipitation of metal oxides.[7] Large rate constants are also important for practical applications (e.g., UO_2 extraction from sea current[8]).

Scheme I



Now we wish to report that the third macrocyclic polyanion, **3**, was newly prepared and it showed satisfactory properties, largest association constant of $10^{20.7}$, and strong characteristic absorption at 265 nm,[9] appropriate for direct analysis of rapid kinetic or precise equilibrium study. Preparation of **3** is rather straightforward as shown in Scheme I.[10] After silica gel chromatographic isolation, **6**$(Ts)_3$ was obtained in 29% yield: mp 103-105 °C; IR (KBr), 1330, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 and 7.6 (AB q, 12 H), 3.0 (t, 12 H), 2.4 (s, 9 H), 1.2-1.6 (m, 42 H). From the crude tosylate, **6** was obtained as a colorless solid in 82% yield by treatment with an alkaline solution followed by extraction: mp 53-54 °C; ^1H NMR δ 2.6 (t, 12 H), 1.3-1.7 (m, 45 H); mass spectrum, *m/e* 423 (M^+), 281, 142. Anal. Calcd for **6**·$2H_2O$: C, 71.05; H, 13.29; N, 9.15%. Found: C, 70.59; H, 13.30; N, 8.87. **3**·Na_3 was obtained as a colorless solid in quantitative yield (NMR determination): IR (neat) 960 cm^{-1}; 60-MHz ^1H NMR (D_2O, hexamethyldisilazane as an external standard) δ 4.1-4.5 (m, 12 H), 1.9-2.4 (m, 12 H), 1.6-1.9 (m, 30 H). 20-MHz ^{13}C NMR (D_2O, dioxane as an internal standard) δ 112.97 from dioxane ($N^{13}CS_2$), -12.01 ($N^{13}C$), -38.1 ($NC^{13}C$), -39.4 ~ -41.2 (other ^{13}C).

The complex between UO_2^{2+} and **3** showed the characteristic absorption. The complex was very stable in the aqueous solution at high pH (7-12),[11] and formation of the UO_2^{2+}·**3** complex was conveniently followed by the characteristic absorption (using the absorption tail at 450 nm). By the spectroscopic determination of the concentration of UO_2^{2+}·**3**, equilibrium constants and rate constants were measured.[12] On the basis of these measurements, association constants were determined both for forward and backward substitution (eq 1) relative to reported association

$$UO_2(CO_3)_3 + 3 \underset{K}{\overset{K}{\rightleftharpoons}} UO_2\cdot 3 + 3CO_3^{2-} \qquad (1)$$

constant for carbonate.[13,14] Both relative constants independently determined are in a good agreement, affording a reliable association constant. This duplicate measurement is necessary for the too strong complexation, since some of dissociation steps easily becomes too slow to allow determination by titration procedure[15]

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(12) Detailed kinetic results will appear in a full-length article.
(13) Reported association constants between UO_2^{2+} and carbonate are spread over a wide range: $10^{23.0}$,[14a] $10^{22.8}$,[14b] $10^{21.5}$,[14a] $10^{20.7}$,[14d] $10^{18.3}$.[14e]
(14) Average value of the four independent and reliable association constants[14c,f,g,h] are chosen to give the value of $10^{21.58\pm0.23}$. Association of UO_2^{2+} with **3** was proven by us as a single step.[12] (a) Paramonova, V. I.; Nikolaeva, N. M. *Radiokhimiya* **1962**, *4*, 84. (b) Klygin, A. E.; Smirnova, Y. D. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 16. (c) Cinneide, S. O.; Scanlan, F. P.; Hynes, M. F. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1013. (d) Babko, A. K.; Kodenskaya, V. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1960**, *5*, 1241. (e) Bullwinkel, E. P. *USAEC* **1954**, RMO-2614. (f) Maya, L. *Inorg. Chem.* **1982**, *21*, 2895. (g) Isymbal, C. *Rapp. CEA-R-Fr., Commis. Energ. At.* **1969**, *CEA-R-3476*. (i) Lemire, R. J.; Tremaine, P. R. *J. Chem. Eng. Data* **1980**, *25*, 361.
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