Table II. Effect of Aging on the Biphasic Vesicular Cleavage of Ellman's Reagent[a]

	percent slow reaction[b]		
age, s[c]	vesicular 16_2[d]	20% cholesterol/ 16_2[e]	18-crown-6/ 16_2[f]
0.046	20.1	25.5	47.6
0.071	*g*	*g*	53.8
0.096	25.5	41.2	61.0
0.146	36.8	54.5	66.1
0.246	45.4	60.0	72.1
0.346	49.7	65.0	81.0
0.446	54.0	66.8	80.9
0.546	58.0	66.9	
0.796	61.1	70.4	
1.05	62.8	71.0	
5.05	64.6	*g*	
10.0	64.6	71.1	
60.0	*g*	*g*	79.0
cosonicate[h]	70.2	66.5	*g*

[a] Conditions as in Table I, note *a*. Method B was used for sequential multimixing of reagents; see Table I, note *b*. [b] The percent of slow reaction was calculated from the absorption change corresponding to the slow process vs. the total absorbance change. The difference between 100% and the tabulated percent slow reaction equals percent fast reaction. [c] Time *between* mixing of 16_2 vesicles with **2** and addition of $S_2O_4^{2-}$. [d] Empty vesicles; Table I, note *g*. [e] Table I, note *h*. [f] Table I, note *i*. [g] Not determined. [h] Reagent **2** was cosonicated with vesicular 16_2 for 5 min at 60 °C and 70 W. 16_2/**2** and dithionite were then mixed in a stopped-flow experiment.

of $S_2O_4^{2-}$ then affords reactions at both sites with different rate constants.[11] This scheme is supported by the variable aging experiments recorded in Table II. When the $16_2 + \mathrm{Ell}_2^{2-}$ solutions are aged 46 ms before $S_2O_4^{2-}$ addition, 80% of the overall reaction is exovesicular (fast) and 20% is subsurface or slow. Increasing the aging time permits more Ell_2^{2-} to reach the subsurface site, and the proportion of the slow reaction increases smoothly to a maximum of ~65% in 1–5 s. The final distribution represents substrate equilibration between exovesicular and subsurface sites; note that cosonication of Ell_2^{2-} with 16_2, followed by stopped-flow reaction with $S_2O_4^{2-}$, affords a similar slow/fast distribution of reactions (Table II).

Indeed, these data give a reasonable fit to integrated equations describing the approach to equilibrium of the (first-order) system $A \rightleftharpoons B$.[12] Analysis gives $k_1 \sim 2.1\ s^{-1}$ and $k_{-1} \sim 1.2\ s^{-1}$, where k_1 represents the exovesicular to subsurface exchange and k_{-1} denotes the reverse process.

Table II reveals that similar phenomena occur with cholesterol-doped 16_2 vesicles and when 18-crown-6 is added to the Ell_2^{2-} solution. In the latter case, the maximum contribution of the slow reaction is significantly greater than in the absence of crown ether and is reached more rapidly. The cholesterol-doped 16_2 vesicles occupy an intermediate position in terms of the maximum contribution of the slow process and the aging time required to achieve it. It should be noted that although aging affects the slow/fast reaction distribution, the rate constants are unaffected.

The catalyzed dithionite cleavages of vesicle-bound Ell_2^{2-} occur at two sites, and equilibration of the substrate between these sites requires ~0.35–~5 s, depending on the experimental conditions. One site is clearly the vesicular surface. The second site probably corresponds to very shallow penetration by Ell_2^{2-} because dithionite ions do not readily cross hydrophobic membranes,[9] and although cholesterol should inhibit endovesicular reactions of $S_2O_4^{2-}$,[13] the data show that the "second-site" reaction is mildly *promoted* by cholesterol.[14]

Accordingly, we consider the second site to be "subsurface", but not "endovesicular". A possible model pictures exovesicular Ell_2^{2-} as initially bound "broadside" (tangentially) on the vesicular surface. With aging of the ensemble, Ell_2^{2-} molecules reversibly migrate to (radial) intercalation sites, between the surfactant monomers, but within the membranes's outer palisade. This location would be less polar than the exovesicular site but still accessible to the dithionite.

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(11) The precise mechanism of the $S_2O_4^{2-}/\mathrm{Ell}_2^{2-}$ reaction is not yet established. In either buffer or vesicular **1**, excess $S_2O_4^{2-}$ generates only 1 equiv of **3** from **2** (as compared to 2 equiv of **3** when dithiothreitol is used). This suggests that aqueous $S_2O_4^{2-}$ may provide nucleophilic HSO_2^-, which cleaves **2** to **3** and $ArSSO_2^-$. Cf.: Castaldi, G.; Perdoncin, G.; Giordano, C. *Tetrahedron Lett.* **1983**, *24*, 2487.

(12) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; pp 185–186, eq 71. We find $(k_1 + k_{-1}) = 3.26\ s^{-1}$, and we take $k_1/k_{-1} = 1.82$ (i.e., 64.6/35.4, Table II, column 2, 5- and 10-s entries).

(13) Moss, R. A.; Hui, Y. *Tetrahedron Lett.* **1983**, *24*, 3961.

(14) Cosonicated 16_2 and Ell_2^{2-} react completely[11] with excluding "hidden" endovesicular Ell_2^{2-}. This suggests relatively free permeability of Ell_2^{2-} (but not dithionite[9]) between "subsurface" and endovesicular sites.

Additions and Corrections

Toward Tricyclo[2.2.2.2]decane. 1. [*n*.2.2.2]Paddlane Systems, *n* = 10–14 [*J. Am. Chem. Soc.* **1983**, *105*, 1656]. PHILIP E. EATON* and BERNARD D. LEIPZIG

Page 1656, the third line of the second paragraph should read as follows: ...gave, after oxidation,...

Polar Radicals. 17. On the Mechanism of Iodine Atom Transfer. A 9-I-2 Intermediate [*J. Am. Chem. Soc.* **1982**, *104*, 3917]. DENNIS D. TANNER,* DARWIN W. REED, and B. P. SETILOANE

Page 3918: Equations 3 and 4 should read

$$[\mathrm{PhI}]/[\mathrm{PhCl}]\cdot[\mathrm{CCl_4}]/[\mathrm{ArI}] = (k_1/k_{\mathrm{Cl}})[1/(k_{-1}/k_2 + 1)] \quad (3)$$

$$(k_1/k_{\mathrm{Cl}})_{\mathrm{obsd}} = k_1/k_{\mathrm{Cl}}[1/(k_{-1}/k_2 + 1)] \quad (4)$$

The plot of the corrected equation, to replace Figure 3, does not show a significant substituent effect for log (k_1/k_{Cl}) as originally reported. The conclusions drawn from this plot must, therefore, be modified. The mechanistic implications of this observation will be the subject of a future communication from this laboratory

Measurement of Nonsynergistic Anion Binding to Transferrin by EPR Difference Spectroscopy [*J. Am. Chem. Soc.* **1982**, *104*, 5775]. DONALD A. FOLAJTAR and N. DENNIS CHASTEEN*

Page 5777: Contrary to our statement that no anion effect is observed when iron(III) nitrilotriacetate 1:2 is used to saturate the protein, subsequent experiments have shown that this is not the case. Anion effects on the EPR spectrum occur when the diferric protein is prepared by using either Fe(II) or Fe(III)–NTA.