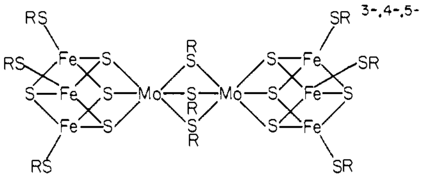
of two-electron transfer to a (protic) substrate. Simple consideration of hydrogen reduction potentials[15] supports this view. Soluble stable molecules that can deliver two electrons at low potentials are uncommon, but recent syntheses of Mo-Fe-S "double-cubane" clusters,[16,17] possible models of the Mo site in nitrogenase,[17] provide an entry to this class of electron carriers. Oxidized cluster **1** (R = Ph[16]) has evidenced no H_2 evolution capability. However, in DMA solution it undergoes successive reversible reductions to $[Mo_2Fe_6S_8(SPh)_9]^{4-}$ (**2**) and $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ (**3**) at half-wave potentials $E_1 = -1.00$ V and $E_2 = -1.21$ V.[11] Anaerobic reaction of a solution of 1 equiv of $(n\text{-}Bu_4N)_3$ (**1**) and 10 equiv of Et_4NBr in acetonitrile with 3 equiv of 0.5 M $Na^+C_{12}H_8^-$ in HMPA followed by cooling to −10 °C afforded, after recrystallization (acetonitrile) of the separated solid, black, extremely air-sensitive crystals of analytically pure $(Et_4N)_5$ (**3**). The larger ^{57}Fe isomer shift[11] of the doubly reduced cluster **3** (0.41 mm/s) vs. **1** (0.32 mm/s) at 80 K signifies increased Fe(II) electronic character in **3** and therewith reduction of its individual clusters.



1 (3–), 2 (4–), 3 (5–)

Reaction systems composed of preisolated $(Et_4N)_5$ (**3**) and excess PhSH in DMA under an argon atmosphere spontaneously evolve H_2[11] and remain homogeneous over the period of reaction. Pertinent H_2 yield and time course results for several systems are shown in Figure 1. Spectrophotometric monitoring of reaction systems such as that in Figure 2 demonstrate that the final cluster species at cessation of H_2 production is **1**. The overall process is proposed to be reaction 2, on which basis H_2 yields are expressed.

$$[Mo_2Fe_6S_8(SPh)_9]^{5-} + 2PhSH \rightarrow [Mo_2Fe_6S_8(SPh)_9]^{3-} + 2PhS^- + H_2 \quad (2)$$

With sufficient ratios X and reaction times H_2 evolution is essentially quantitative (Figure 1). Thus in the system with X = 379:1 after 10 h and in those with X = 266–532:1 after 24 h, 85% and 93–98%, respectively, of the theoretical amount of H_2 based on the two-electron oxidation of **3** are produced. In comparison, 1.03 and 1.10 mM solutions of the one-electron reductant **2**, generated by the stoichiometric reaction $\mathbf{1} + \mathbf{3} \rightleftarrows 2\,\mathbf{2}$ ($K_{equil} = 10^{3.55}$ from $E_{1,2}$) with X = 379:1, reacted more slowly and less efficiently. After ~70 min (vs. 20 min for the comparable system containing 1.14 mM **3**) a 50% H_2 yield was obtained, which increased to only ~60% after 16 h, although oxidation of **2** to **1** was complete.[13] It is possible that some of the H_2 evolved originates from a rapid pathway involving the small amount (initially ~1.5%) of **3** present in the equilibrium mixture.

The foregoing results demonstrate that one sufficient condition for homogeneous, essentially quantitative H_2 evolution is utilization of a low potential two-electron reductant[18] which, inter alia, may be capable of stabilizing hydride at a metal site. The variation in behavior between $[Fe_4S_4(SPh)_4]^{3-}$ and **3** is unlikely to arise from different one-electron reducing abilities inasmuch as their first reduction potentials differ by only 14 mV in DMA solution.[11] Further research will involve kinetic studies of **3** and other reduced clusters with thiols, other acids, and additional two-electron substrates. Present results indicate that **3** can produce H_2 from other thiols (e.g., 79% yield from $PhCH_2SH$ after 24 h with X = 430:1) but less satisfactorily from certain other acids such as HOAc (25% after 20 h with X = 1100:1) which may also effect ligand substitution, observed with Fe–S clusters,[10] and/or cluster degradation.

Acknowledgment. This research was supported by National Science Foundation Grant No. CHE 77-04397. We thank Dr. R. B. Frankel for the Mössbauer measurements.

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(15) At pH 7: $H^+ + e^- \rightarrow H$, −2.5 V; $2H^+ + 2e^- \rightarrow H_2$, −0.41 V.

(16) G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, **740** (1978); G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, in press.

(17) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979); T. E. Wolff, P. P. Power, R. B. Frankel, and R. H. Holm, *ibid.*, **102**, 4694 (1980).

(18) H_2 evolution from H_2O in a heterogeneous system containing the two-electron reductant $Ru(bipy)_3{}^0$ has recently been demonstrated: H. D. Abruña, A. Y. Teng, G. J. Samuels, and T. J. Meyer, *J. Am. Chem. Soc.*, **101**, 6745 (1979).

(19) U.K. Science Research Council/NATO Postdoctoral Fellow, 1980.

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Ion Pairing and Solvent Effects in the Reactivity of Anions toward Free Radicals[1]

Sir:

We have reported that the photostimulated $S_{RN}1$ reaction (Scheme I) between 2-chloro-2-nitropropane and enolate anions is sensitive to the nature of the solvent and the counterion.[2] Since it is often dangerous to infer reactivity from the rate or yield of a radical chain process, we have examined the relative reactivity of a series of anions in competitive $S_{RN}1$ reactions to ascertain the importance of ion-pairing effects (Scheme II). Relative reactivities of the anions (k_A/k_B) toward the intermediate 2-nitro-2-propyl radicals were evaluated from product analysis.[3]

Scheme I. $S_{RN}1$ Mechanism

$$Me_2C(X)NO_2^{-}\cdot \rightarrow Me_2\dot{C}NO_2 + X^-$$

$$Me_2\dot{C}NO_2 + A^- \rightarrow Me_2C(NO_2)A^{-}\cdot$$

$$Me_2C(NO_2)A^{-}\cdot + Me_2C(X)NO_2 \rightarrow Me_2C(NO_2)A + Me_2C(X)NO_2^{-}\cdot$$

$$X = Cl,\ p\text{-}MePhSO_2,\ NO_2$$

Scheme II. Competitive $S_{RN}1$ Reactions

$$Me_2\dot{C}NO_2 + A^- \xrightarrow{k_A} Me_2C(NO_2)A^{-}\cdot \xrightarrow{-e^-} Me_2C(NO_2)A$$

$$Me_2\dot{C}NO_2 + B^- \xrightarrow{k_B} Me_2C(NO_2)B^{-}\cdot \xrightarrow{-e^-} Me_2C(NO_2)B$$

$$A^-, B^- = Me_2C{=}NO_2^-,\ (EtO_2C)_2CH^-,\ (EtO_2C)_2CMe^-,\ (EtO)_2PO^-,\ (EtO)_2PS^-$$

Table I gives the relative reactivities[4] of a series of anions relative to $Me_2C{=}NO_2^-$ in the presence of K^+[2.2.2]-cryptand

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(1) Electron Transfer Processes. 23. This work was supported by Grant CHE-7823866 from the National Science Foundation.

(2) Russell, G. A.; Jawdosiuk, M.; Ros, F. *J. Am. Chem. Soc.* **1979**, *101*, 3378.

(3) Pure samples of the products (2,3-dimethyl-2,3-dinitrobutane, diethyl methyl(2-nitroisopropyl)malonate, diethyl isopropylidenemalonate, diethyl 2-nitroisopropylphosphonate, and diethyl 2-nitroisopropylthiophosphonate) were used as references for ^1H NMR analysis. A molar ratio of $Me_2C(X)NO_2{:}A^-{:}B^-$ of 1:1:1 was generally used. The anions were generated in situ with equivalent amounts of lithium or potassium *tert*-butoxide. Reactions were conducted at 25 °C with sunlamp irradiation and were complete in 90 min. The overall yields of products were usually 80–100%.

(4) By use of the integrated equation, $k_A/k_B = \log(1 - [P_A]/[A^-]_0)/\log(1 - [P_B]/[B^-]_0)$. With A^- equal to $(EtO_2C)_2CH^-$, a molar ratio of $Me_2C(X)NO_2{:}A^-{:}B^-$ of 1:2:1 was employed in order to eliminate participation of $B^- = Me_2C{=}NO_2^-$ in the elimination of HNO_2 from the intermediate diethyl (2-nitroisopropyl)malonate. In this case the rate expression employed was $k_A/k_B = \log(1 - [EtO_2C)_2C{=}CMe_2]/2[(EtO_2C)_2CH^-]_0)/[2\log(1 - [O_2NCMe_2CMe_2NO_2]/[Me_2C{=}NO_2^-]_0)]$.

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Table I. Relative Reactivities of Anions toward 2-Nitro-2-propyl Radical in Me_2SO at 25 °C[a]

anion	K^+[2.2.2]-cryptand[b]	0.2 M Li^+	1.0 M Li^+ [c]
$(EtO_2C)_2C(Me)^-$	10[d]	0.24[e]	0.44[e]
$(EtO_2C)_2CH^-$	6.0	0.47[f]	0.95
$Me_2C{=}NO_2^-$	1	1	1
$(EtO)_2PO^-$	0.54	0	0
$(EtO)_2PS^-$	0.90[g]	1.2	0.82

[a] Except as otherwise noted 2-(*p*-tolylsulfonyl)-2-nitropropane was used as a precursor of 2-nitro-2-propyl radical; all anions were run in competition with $Me_2C{=}NO_2^-$. [b] $[K^+] = 0.15$ M; molar ratio K^+:[2.2.2]-cryptand = 1:1. [c] [LiI] = 0.8 M. [d] With 2-chloro-2-nitropropane, $k_{(EtO_2C)_2C(Me)^-}/k_{Me_2C=NO_2^-} = 11$. [e] Average of 2-chloro-, 2-(*p*-tolylsulfonyl)-, and 2-nitro-2-nitropropane; mean deviation: ±0.02. [f] $k_{(EtO_2C)_2CH^-}/k_{(EtO_2C)_2C(Me)^-} = 2.0$. [g] $k_{(EtO)_2PS^-}/k_{(EtO)_2PO^-} = 2.0$.

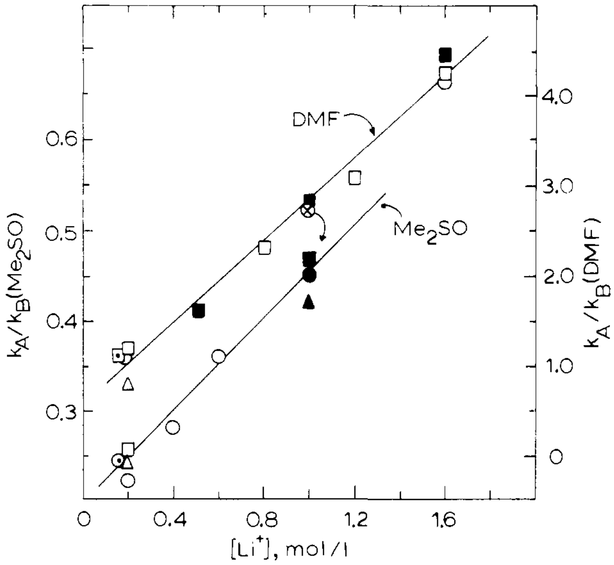

Figure 1. Relative reactivities of $(EtO_2C)_2C(Me)^-$ (=A) and $Me_2C{=}NO_2^-$ (=B) toward 2-nitro-2-propyl in Me_2SO and DMF as a function of $[Li^+]$; ○, = 2-*p*-tolylsulfonyl-2-nitropropane, □, = 2-chloro-2-nitropropane, △ = 2,2-dinitropropane. For open symbols, $[A^-] = [B^-] = [Li^+]/2$; for filled symbols, $[A^-] = [B^-] = 0.1$ M, excess LiI added; ⊙, 0.8 M $Bu_4N^+ClO_4^-$ added; ⊗, 0.8 M $LiClO_4$ added.

and Li^+ as counterions in Me_2SO. Consistent values were obtained with the three leaving groups (X = Cl, p-$MePhSO_2$, NO_2) and also by the competitive experiments between the anion pairs $(EtO_2C)_2CH^-$ vs. $(EtO_2C)_2CMe^-$, $(EtO)_2PO^-$ vs. $(EtO_2C)_2CMe^-$, and $(EtO)_2PS^-$ vs. $(EtO)_2PO^-$. By changing the counterions, the relative reactivities of malonate and nitronate anions can be dramatically reversed, e.g., $k_{methylmalonate}/k_{nitronate} = 10$ with K^+[2.2.2]-cryptand, but 0.24 in the presence of 0.2 M Li^+. Lithium diethyl phosphite shows no detectable reactivity relative to the lithium nitronate, whereas with K^+[2.2.2]-cryptand as the counterion the reactivities of the phosphite and nitronate anions are comparable.[5] With the diethyl thiophosphite anion, there is no appreciable change in the relative reactivity toward the nitronate anion when the cation is varied.

The relative reactivities of the lithium salts of diethyl methylmalonate and 2-nitropropane in Me_2SO or DMF are affected by changes in the Li^+ concentration by dilution or the addition of LiI or $LiClO_4$ (Figure 1). Addition of a large excess of $Bu_4N^+ClO_4^-$ did not affect the rate ratio, which is also independent of the leaving group, within experimental error. We interpret the variations observed as due to changes in the overall reactivities of the anions by varying degrees of ionic association as $[Li^+]$ changes. The relative reactivities of the methylmalonate and nitronate anions in Me_2SO decrease from 10:1 in the presence of K^+ (cryptand) to 0.25:1 in the presence of 0.2 M Li^+ and then increase to ~0.5:1 at 1 M Li^+. We conclude that the free ions and ion pairs can have drastically different (and even reversed) relative reactivities.[6] With K^+[2.2.2]-cryptand in Me_2SO, the degree of dissociation of the malonate salts should be high.[7] With Li^+, however, they are extensively associated[7] and presumably less reactive. Addition of further Li^+ may not affect the reactivity of the malonate anion ($k_{(EtO_2C)_2CMe^-}/k_{(EtO_2C)CH^-}$ is insensitive to excess LiI), but ion pairing may decrease the reactivity of the nitronate anion.[8] Thus, under controlled conditions, the rate of the photostimulated coupling of p-$MePhSO_2CMe_2NO_2$ with $Me_2C(NO_2)Li$ in Me_2SO is appreciably slower in the presence of excess LiI, whereas such an effect is not observed in the corresponding reaction with $(EtO_2C)_2C(Me)Li$.

Table II. Relative Reactivity of Anions of Diethyl Methylmalonate and 2-Nitropropane in Different Solvents at 25 °C[a]

counterion, M	solvent	$k_{(EtO_2C)_2C(Me)^-}/k_{Me_2C=NO_2^-}$
Li^+, 0.2	HMPA	0.22
Li^+, 0.2	Me_2SO	0.26
Li^+, 0.2	DMF	1.3
Li^+, 0.2	THF–DMF (50:50)	1.9
Li^+, 0.2	THF–DMF (90:10)	18
Li^+, 0.2	THF	>70
Li^+[12]-crown-4, 0.2	THF	20
K^+[2.2.2]-cryptand, 0.15	Me_2SO	11
K^+[2.2.2]-cryptand, 0.15	THF–Me_2SO (90:10)	1.6
K^+[2.2.2]-cryptand, 0.15	THF	0.39

[a] 2-Chloro-2-nitropropane was used as a substrate.

A change in solvent from HMPA, Me_2SO, or DMF to the less polar THF has a striking effect on the relative reactivity of the lithium salts of diethyl methylmalonate and 2-nitropropane (Table II). The ratio (0.2 M Li^+) increases with decreasing solvating power of the solvent (e.g., from 0.22:1 in HMPA to >70:1 in THF). This change in relative reactivity may be associated with an increase in ion pairing and a decrease in reactivity of the nitronate anion as the polarity of the solvent decreases. With K^+[2.2.2]-cryptand in THF, some degree of ionic association probably exists,[9] and it may be responsible for the different rate ratios observed with K^+[2.2.2]-cryptand in THF and Me_2SO ($k_{(EtO_2C)_2CMe^-}/k_{Me_2C=NO_2^-} = 0.4$ (THF); 11 (Me_2SO)). On the other hand, solvent effects may play a role on the reactivity of the free anions.[10,11]

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(5) Lithium diethyl phosphite is presumably highly associated in Me_2SO since in diylyme only ion pairs seem to exist: Moedritzer, K. *J. Inorg. Nucl. Chem.* **1961**, *22*, 19.

(6) Ion pairing can also affect the nature of the reaction between an anion and a radical. Thus with enolate anions of simple ketones, addition of the 2-nitro-2-propyl radical according to the $S_{RN}1$ scheme occurs only with lithium counterion in nonpolar solvents such as THF.[2] In Me_2SO with Li^+ or K^+ products of the $S_{RN}1$ reaction are not observed.

(7) Values of K_{diss} of alkali metal salts of dimethyl methylmalonate in Me_2SO at 25 °C are 3.5×10^{-5} for Li^+ and 4.9×10^{-3} for K^+: Arnett, E. M.; DePalma, V.; Maroldo, S.; Small, L. S. *Pure Appl. Chem.* **1979**, *51*, 131.

(8) These results suggest that K_{diss} of lithium nitronates is greater than the lithiomalonates. This is not unreasonable in view of the chelating abilities of the anions of β-dicarbonyl compounds: Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737.

(9) Cambillau, C.; Sarthou, P.; Bram, G. *Tetrahedron Lett.* **1976**, 281.

(10) Small amounts of *tert*-butyl alcohol do not affect the observed relative reactivities of the anions of diethyl methylmalonate and $Me_2C{=}NO_2^-$. Using $KOCMe_3$ and KNH_2 as bases in THF in the presence of [2.2.2]-cryptand yielded values of $k_{malonate}/k_{nitronate}$ of 0.4 and 0.2, respectively. With $LiOCMe_3$ as the base in Me_2SO and Me_2SO–EtOH (90:10), values were 0.24 and 0.20, respectively. It has been shown that small amounts of water have a negligible effect on the rate of alkylation of potassium enolates of some β-diketones by MeI in Me_2SO: DePalma, V. M.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 3514.

(11) Solvent effects on the rate of the $S_{RN}1$ reaction of $CH_3COCH_2^-K^+$ with 2-chloroquinoline have been reported: Moon, M. P.; Wolfe, J. F. *J. Org. Chem.* **1979**, *44*, 4081.

The following are other examples that show the sensitivity of photostimulated $S_{RN}1$ reactions to the nature of the solvent and counterion. The reaction between 2-chloro-2-nitropropane and ethyl sodioacetylacetate in DMF yields ethyl 2-isopropylideneacetylacetate, but no reaction takes place with Li^+ in THF; potassium diethyl phosphite and 2-(*p*-tolylsulfonyl)-2-nitropropane in THF yield diethyl 2-nitroisopropylphosphate,[12] but no reaction occurs with Li^+ in THF; potassium diethyl thiophosphite reacts with 2-(*p*-tolylsulfonyl)-2-nitropropane in Me_2SO to give diethyl 2-nitroisopropylthiophosphonate, but with Li^+ in THF, the starting sulfone is recovered.

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[12] Russell, G. A.; Hershberger, J. *J. Chem. Soc., Chem. Commun.* **1980**, 216.

[13] Postdoctoral Fellow of the Consejo Superior de Investigaciones Cientificas de Espana, 1979–81.

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Substitution Reactions of Vinylmercurials by a Free-Radical Chain Mechanism[1]

Sir:

We have found that 1-alkenylmercury halides readily undergo photostimulated free-radical chain substitution reactions 1–3 (X = Cl, Br, OAc). In all cases the reactions are completely inhibited

$$\mathrm{RCH{=}CHHgX + R'Y{-}YR' \xrightarrow{h\nu} RCH{=}CHYR' + XHgYR'} \qquad (1)$$

$$\mathrm{Y = S,\ R' = alkyl\ or\ aryl;\quad Y = Se,\ Te,\ R' = phenyl}$$

$$\mathrm{RCH{=}CHHgX + Z{-}Q \xrightarrow{h\nu} RCH{=}CHZ + XHgQ} \qquad (2)$$

$$\mathrm{Z = PhSO_2,\ Q = Cl;\ Z = Me_2CH,\ Q = I}$$

$$\mathrm{RCH{=}CHHgX + A^- \xrightarrow{h\nu} RCH{=}CHA + Hg^0 + X^-} \qquad (3)$$

$$\mathrm{A^- = (RO)_2PO^-,\ PhP(OBu)O^-,\ AlkSO_2^-,^2\ ArSO_2^-,^2\ AlkS^-,\ ArS^-}$$

by 5–10 mol % of di-*tert*-butyl nitroxide or galvinoxyl and fail to proceed significantly in the dark.

Reactions 1 and 2 or 3 with $A^- = RS^-$ clearly proceed by a free-radical addition–elimination mechanism (Scheme I).

In reaction 2 a vinyl radical intermediate is clearly excluded by the complete absence of the vinyl choride when the reactant is $PhSO_2Cl$ and only traces of the vinyl iodide when the reactant is Me_2CHI. A vinyl radical would attack these substrates to give halogen atom transfer. Furthermore, reactions 1, 2, or 3 with $A^- = RSO_2^-$ or RS^- fail to occur with phenyl- or benzylmercurials. This excludes reaction 1 occurring by the S_H2 attack of a carbon-centered radical on R′YYR′ or reaction 3 occurring by the $S_{RN}1$ mechanism.[2] Moreover, reaction 1 with Y = S will occur in PhH in the presence of 1 equiv of 2,6-di-*tert*-butylphenol to yield the vinyl sulfide in nearly quantitative yield with but a slight rate retardation.

In reaction 3 with $A^- = PhS^-$ the reaction is inhibited by an excess of the mercaptide ion.[3] However, the reaction is not inhibited by the presence of the free mercaptan, and the vinyl sulfide is still formed in nearly quantitative yield (the reaction is most conveniently performed by sunlamp irradiation of the alkenylmercury chloride and mercaptan in PhH in the presence of excess $NaHCO_3$). Again, a vinyl radical intermediate is excluded since this would have reacted with the mercaptan to form the olefin by hydrogen transfer. In reaction 3 with $A^- = R'S^-$, ligand exchange occurs readily to form the 1-alkenylmercury mercaptide (RCH=CHHgSR′), which can be isolated from solutions containing a trace of di-*tert*-butyl nitroxide. The pure mercaptide when irradiated in a variety of solvents (PhH, Et_2O, Me_2SO) decomposes cleanly according to reaction 4; again the mercaptide ion inhibits the reaction while the free mercaptan has no effect on the rate or product. The decomposition of RCH=CHHgSR′ follows Scheme I, probably with the stepwise expulsion of Hg^0 from the intermediate *β*-mercurio radical.[3,4]

$$\mathrm{RCH{=}CHHgSR' \xrightarrow{h\nu} RCH{=}CHSR' + Hg^0} \qquad (4)$$

Table I gives some typical yields observed in these reactions. The processes are not completely stereoselective, which is consistent with Scheme I. With R = *tert*-butyl only the *E* products have been observed (*E*/*Z* > 20:1), but with smaller substituents (R = Ph, *n*-Pr) mixtures of the *E* and *Z* isomers are formed (Table I).

In an analogous series of reactions divinylmercurials undergo a photostimulated reaction with aryl disulfides (but not with primary alkyl disulfides) to form the vinyl sulfides (reaction 5).[5]

$$\mathrm{[(Ph)_2C{=}CH]_2Hg + PhSSPh \xrightarrow[PhH]{h\nu,\ 3\ h} \underset{99\%}{2(Ph)_2C{=}CHSPh} + Hg^0} \qquad (5)$$

At 0 °C in PhH–hexane solution the bis(vinyl)mecurial does not undergo significant electrophilic cleavage by PhSH, a dark reaction which occurs readily in Me_2SO or PhH at 25 °C. At 0 °C in PhH–hexane the presence of PhSH had no effect on the rate of reaction 5 and the vinyl sulfide was formed in quantitative yield. The reaction is, however, strongly inhibited by 5 mol % of galvinoxyl. We thus conclude that reaction 5 also does not involve intermediate vinyl radicals and chain propagation occurs by Scheme I followed by reactions 6 and 4. The failure of alkyl

$$\mathrm{(Ph)_2C{=}CHHg\ (from\ Scheme\ I) + PhSSPh \rightarrow (Ph)_2C{=}CHgSPh + PhS\cdot} \qquad (6)$$

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[1] Electron Transfer Reactions. 24. This work was supported by Grant CHE-7823866 from the National Science Foundation.

[2] Hershberger, J.; Russell, G. A. *Synthesis* 1980, 475.

[3] The inhibition by the thiolate anion may involve the trapping of the chain-carrying species HgSR (Scheme I). Trapping of RS· seems to be eliminated by the observation that PhS^- is not an inhibitor in reaction 5 where the intermediate Hg species can react rapidly with PhSSPh.

[4] The mercury substituent probably stabilizes the intermediate *β*-mercurio radical, leading to regioselectivity in the first step of Scheme I. It has been reported that a mercury substituent greatly activates *β*-hydrogen atoms toward attack by the trichloromethyl radical [Kochi, J. K.; Nugent, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 5406], although no dramatic activation has been noted in hydrogen abstraction by the less selective and less electrophilic phenyl radical in attack upon diethylmercury [unpublished results with J. D. Hunt].

[5] A number of thermal substitution reactions of $(CH_2{=}CH)_2Hg$ have been reported [Foster, D. J.; Tobler, E. *J. Am. Chem. Soc.* **1961**, *83*, 851; *J. Org. Chem.* **1962**, *27*, 834; U.S. Patents 3 087 952, April 30, 1963; Feb 15, 1966; 3 090 814, May 21, 1963; 3 153 074, Dec 23, 1963. Tobler, E.; Foster, D. J. *Z. Naturforsch.* **1962**, *176*, 135, 136] which follow the stoichiometry

$$\mathrm{(CH_2{=}CH)_2Hg + HX \xrightarrow{\Delta} CH_2{=}CH_2 + CH_2{=}CHX + Hg^0}$$

where X = SR, SC(=O)CH_3, OPh, O_2CR, O_2SPhMe-*p*. This work has been extended to include $X^- = (EtO)_2P({=}O)O^-$, $MeP({=}O)(OR)O^-$, $(RO)_2P({=}S)S^-$ [Gololobov, Y. G.; Domitrieva, T. F.; Suborovskii, L. Z. *Probl. Organ. Sintoza, Akad. Nauk, SSSR, Otd. Obshsh. Tekhn. Khim* **1965**, 314; *Chem. Abstr.* **1966**, *64*, 6683h] and at 180 °C in the presence of hydroquinone, $C_nF_{2n+1}CO_2^-$ and $(CF_3)_2C{=}NO^-$ [Sterlin, R. N.; Euplov, B. N.; Knunyantz, I. L. *Zh. Vses. Khim. Obshchest.* **1967**, *12*, 591; *Chem. Abstr.* **1968**, *68*, 49706c]. It appears likely that some of these processes *may* proceed by a free-radical decomposition of the intermediate $CH_2{=}CHHgX$ formed by electrophilic cleavage of divinylmercury. In the present work $CH_2{=}CHHgCl$ failed to give a photostimulated substitution reaction with anions such as $(EtO)_2PO^-$ or RSO_2^-, but led instead to polymeric products. Foster and Tobler also report the thermal decompositions of $CH_2{=}CHHgSPh$, $CH_2{=}CHHgO_2CR$, $R'CH{=}CR'HgO_2CR$, and $CH_2{=}CHHgSCN$ to $CH_2{=}CHSPH$, $CH_2{=}CHOC({=}O)CH_3$, $CH_2{=}CHOC({=}O)Ph$, $R'CH{=}CR'O_2CCH_3$, $CH_2{=}CHSCN$, and $CH_2{=}CHNCS$ at 100–200 °C. At 35 °C, (*E*)-$Me_3CCH{=}CHHgOAc$ does not undergo decomposition to yield the vinyl acetate even with prolonged irradiation at 350 nm.

0002-7863/80/1502-7603$01.00/0