pholine and triethylamine were satisfactory. These observations are consistent with the view that thiolate acts as a nucleophilic agent in an S_N2 attack on carbon. All of the demethylation reactions gave only one nucleotidic product with no traces of material derived from S_N2 attack at $C_{5'}$.

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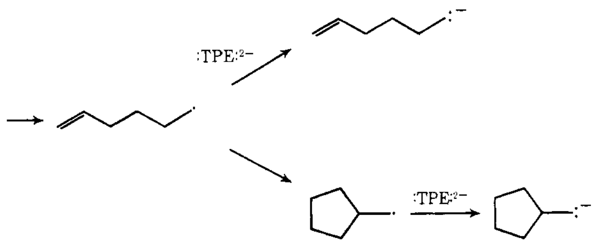
Halogen Effects in Electron-Transfer Reactions of Alkyl Halides with Disodium Tetraphenylethylene. Do Alkyl Halide Anion-Radicals Have Finite Lifetimes in Solution?

Sir:

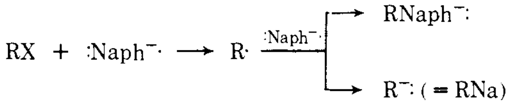
In 2-methyltetrahydrofuran at room temperature, disodium tetraphenylethylene ($:TPE:^{2-}$) at initial concentrations 1–3 × 10^{-2} M reacts with 5-hexenyl chloride, bromide, and iodide to give both 1-hexene and methylcyclopentane, with 1-hexene/methylcyclopentane = 0.2–0.6.[1,2] In the same solvent, sodium metal reacts with 5-hexenyl chloride to give both products with 1-hexene/methylcyclopentane = 10–13. Thus, the great majority of the cyclization found in the $:TPE:^{2-}$ reactions cannot be attributed to cyclization of intermediate 5-hexenylsodium. That it is due instead to cyclization of intermediate 5-hexenyl radicals is confirmed by the observation that the ratio 1-hexene/methylcyclopentane decreases from 0.6 to 0.02 as the initial concentration of $:TPE:^{2-}$ is varied from 3×10^{-2} M down to 1×10^{-3} M. This is consistent with the competition shown in eq 1, and the observations are in quantitative agreement with this scheme for 12 experiments spanning the concentration range given.[1] Further, *tert*-pentyl chloride reacts more rapidly with $:TPE:^{2-}$ than pentyl chloride, yet *tert*-pentyl chloride gives only 9% olefins; no traces of olefins are found from pentyl chloride. Thus, the initial steps of these reactions cannot have significant components of nucleophilic displacement and elimination. Electron transfer giving intermediate alkyl radicals R· from alkyl halides RX is occurring instead.



(1)

This is all parallel to previous findings for the related reactions of alkyl halides with sodium naphthalene ($:Naph^{-}\cdot$).[4] The parallel ceases with the consideration of halogen effects on product yields. In reactions with sodium naphthalene, the yield of reduction products (those derived from intermediate alkylsodiums RNa, as opposed to "alkylation" products) is halogen independent (X = I, Br, Cl, F).[4,5] In reactions with disodium tetraphenylethylene in 2-methyltetrahydrofuran, primary alkyl iodides give 66 ± 3% reduction products, while bromides give 52 ± 3% and chlorides give 34 ± 5%.[6]

The important part of the mechanism for the alkyl halide–sodium naphthalene reaction is presented in eq 2.[4] There is no halogen effect because the C–X bond is broken before the product-partitioning steps. By similar reasoning, the analogous initial step for reactions of disodium tetraphenylethylene will also predict no halogen effect (eq 3).



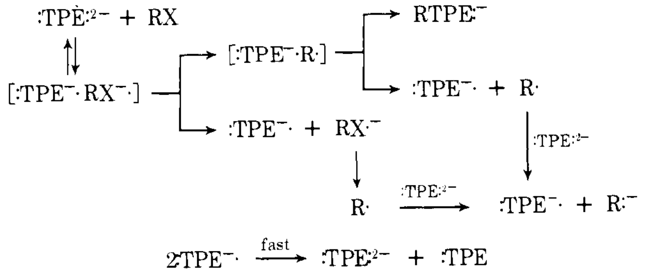
(2)

$$RX + :TPE:^{2-} \rightarrow [:TPE^{-}\cdot\ R\cdot] \qquad (3)$$

Here the brackets indicate a geminate radical pair that has not suffered permanent separation by relative diffusion.[7-9] The finding of a distinct halogen effect requires a special explanation.

If the alkyl halide anion-radical $RX^{-}\cdot$ is introduced as an intermediate of finite lifetime in a scheme that is a simple extension of eq 2 to the case of a reactant dianion, Scheme I, then a prediction of a halogen effect can be made. Here the halogen dependence arises in the competition between the decomposition of $RX^{-}\cdot$ in the geminate radical pair $[:TPE^{-}\cdot\ RX^{-}\cdot]$ and the diffusive separation of this pair. The longer the lifetime of $RX^{-}\cdot$, the greater the fraction of radical pairs $[:TPE^{-}\cdot\ RX^{-}\cdot]$ that suffer permanent separation and thereby give reduction product ultimately, rather than the alkylation product that results from cage reactions.[10] This explanation requires that $RX^{-}\cdot$ lifetimes be sufficient to permit a significant competition with permanent diffusive separation of the geminate radicals. If typical diffusion parameters apply, rate constants for $RX^{-}\cdot$ must be near 10^{10} s^{-1}.[7-9]

Scheme I



Counterions are omitted above, but aggregation must be at least to the ion pair and neutral triple ion stage. The disproportionation of sodium tetraphenylethylene in 2-methyltetrahydrofuran lies far to the right ($:TPE:^{2-}$) side at equilibrium. ESR measurements of $[:TPE\cdot^{-}]$ indicate that it is about 10^{-6} M during a typical reaction.

The most viable alternative to invoking $RX^{-}\cdot$ to account for our data is to suppose that the presence of NaX in the "cage" [Na^+ :$TPE^{-}\cdot$ R· Na^+X^-] somehow affects the subsequent chemistry. Perhaps the most likely possibility is that ionic aggregation of NaX with sodium tetraphenylethylene species affects their reactivities. We have sought such effects by saturating :TPE:$^{2-}$ solutions with NaI prior to reactions with 5-hexenyl chloride and 5-hexenyl iodide.[11] In each case the reduction product yield (RCl, 29%; RI, 63%) was within experimental error of the value obtained without added NaI. Thus, this alternative to $RX^{-}\cdot$ is weakened.

When $RX^{-}\cdot$ escapes its geminate radical partner or is generated without a geminate radical partner (as in :$Naph^{-}\cdot$ reactions), its inevitable fate will be decomposition to R·.[12] Thus, halogen effects will vanish in such cases.

We have been able to find in the literature very little evidence for or against alkyl halide anion-radicals as species of finite lifetimes in solution.[13,14] Our results are strongly suggestive, but not definitive, since a less attractive alternative hypothesis has not been definitely ruled out. However, our data suggest that future probes for $RX^{-}\cdot$ with alkali metal counterions in ethers should be designed to detect species with lifetimes near 10^{-10} s.

Acknowledgment. This work was supported by grants from the National Science Foundation.

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(2) The experimental techniques were the same as in earlier works.[3] Analyses were by VPC using internal standards. 2-Methyltetrahydrofuran was chosen as the solvent because if affords adequate solubility and a large disproportionation equilibrium constant for NaTPE: 2NaTPE $\rightleftarrows$ Na_2TPE + TPE. ESR measurements indicate that [NATPE = :$TPE^{-}\cdot$] was about 10^{-6} M during our experiments, minimizing its chemical significance except in radical cage reactions (see Scheme I).

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(10) That :$TPE^{-}\cdot$ reacts with alkyl radicals to give almost exclusively alkylation products, as in Scheme I, was verified in studies of NaTPE reactions with alkyl halides in solvents where its disproportionation is not greatly favored.[1]

(11) NaI was generated in situ by the reaction of I_2 with :TPE:$^{2-}$ in 2-methyltetrahydrofuran.

(12) If the rate constant for decomposition of $RX^{-}\cdot$ is 10^{10} s^{-1}, as our data indicate, and if the rate constant for encounters is 10^{10} M s^{-1}, then for solutions 0.1 M or less in a potential reactant with $RX^{-}\cdot$, the decomposition of the latter will be at least ten times faster than *encounters*, much less reactions, with the potential reactant.

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(14) Data of P. P. Infelta and R. H. Schuler, *J. Phys. Chem.*, **76,** 987 (1972), from radiolyses of cyclohexane solutions of alkyl halides, can be interpreted in terms of a methyl chloride anion-radical with a lifetime near 3×10^{-8} s and a methyl bromide anion-radical with a lifetime not greater than 3×10^{-9} s. We are grateful to an anonymous referee for drawing our attention to this work. Our work implies halogen effects in the opposite order, i.e., longest lifetimes for alkyl iodide anion-radicals. However, the leaving groups in our systems are better viewed as sodium halide ion pairs NaX than as halide ions.

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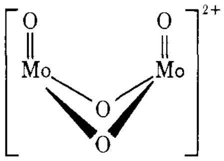
A Triply Bridged Binuclear Molybdenum(V) Compound Containing Two Kinds of Bridging Thiophenolate Groups

Sir:

The suggestion that one or more S atoms may be coordinated to molybdenum in molybdoenzymes has resulted in considerable interest in the coordination chemistry of molybdenum compounds of sulfur-containing ligands.[1] As part of our general studies of the synthesis, structure, and reactivity of molybdenum compounds, we have been investigating the reactions of complexes containing the $[Mo_2O_4]^{2+}$ core (**1**) with thiols.[2-6] Previous chemical and spectroscopic studies of some of the products of these reactions[2,4] led to the prediction that those compounds of stoichiometry $Mo_2O_3(SR')_2(S_2CNR_2)_2$ (**2**) contained a bridging oxo group and two bridging SR′ groups. Support for this concept came from the study of the reaction of an oxinato complex of **1** with 2-mercaptoethanol, which provided the first structurally defined example of a triply bridged binuclear Mo(V) complex.[7] Herein, we confirm stoichiometry **2** for R′ = Ph and R = Et by an x-ray structure determination and show that this red-orange diamagnetic product of the reaction[2,4] of $Mo_2O_4(S_2CNEt_2)_2$ (**3**)[3,8] with excess thiophenol is a triply bridged complex which contains two strikingly different bridging thiophenolate groups.



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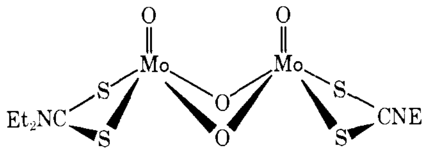

3

A sample of $Mo_2O_3(SPh)_2(S_2CNEt_2)_2$ (**4**) was prepared as previously described,[4] and single crystals were obtained from acetone. Preliminary precession photographs (Mo Kα) established that the crystals were triclinic with a = 9.352 (3), b = 19.245 (9), c = 21.426 (7) Å, α = 112.78 (2), β = 119.10 (2), and γ = 80.00 (3)°. Space group $P\bar{1}$ was assumed and confirmed by successful refinement of the structure. The calculated and observed densities (1.68 and 1.66 g cm^{-3}, respectively) were consistent with four molecules of **4** and one molecule of acetone per unit cell. This formulation required

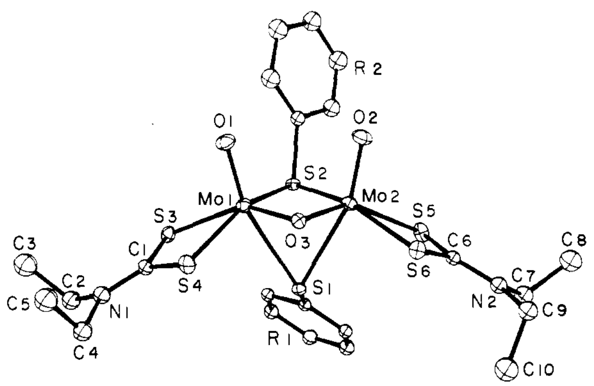

Figure 1. Perspective view of one of the molecules of **4**. The other molecule of **4** in the asymmetric unit has the same coordination environment about the Mo atoms, but slightly different conformations of the ethyl groups of the dithiocarbamate ligands.