

the observation of two new, corresponding signals<sup>12</sup> of **4** (b in **4a**). On the other hand, **3** and **4** behave like enantiomers in their chiroptical properties with respect to nickel, i.e.  $[\theta]_{630}$  ca.  $-1190$  and  $+1260$ . Therefore, the diastereomerization **3**  $\rightarrow$  **4** can also be monitored by time-dependent circular dichroism (mutarotation). The interconversion rates are cleanly first order for **3** in tetralin solution; both methods define a common Eyring plot with  $\Delta H^\ddagger = 22.5 (\pm 0.8)$  kcal/mol and  $\Delta S^\ddagger = -15 (\pm 3)$  cal K<sup>-1</sup> mol<sup>-1</sup>. The  $\Delta G^\ddagger$  values of 27.0 (at room temperature) or 29.3 kcal/mol (at 453 K for comparison with **1**) thus confirm the lower limit<sup>2</sup> of  $\geq 21.8$  kcal/mol for **1** ( $R^1 = C_6H_5$ ,  $R^2 = CH_3$ ,  $R^3 = C_2H_5$ ).

Does the bulky bornane skeleton perturb such barriers? We measured the inversion **5**  $\rightleftharpoons$  **6** for comparison with the known<sup>2</sup> activation enthalpy 17.3 kcal/mol (at 358 K in cyclohexane) of **1** ( $R^1 = R^2 = CH_3$ ,  $R^3 = C_2H_5$ ). Both processes are fast on the NMR time scale and can be followed by coalescence studies on several pairs of diastereotopic protons. Although **5-6** is too sensitive to be isolated in pure form, its very large and characteristic chemical <sup>1</sup>H NMR shifts permit the easy evaluation of  $\Delta G^\ddagger = 17 (\pm 1)$  kcal/mol (at 345 K in benzene-tetralin). Thus at least for  $R^1 = CH_3$  the comparison of **5-6** with the above **1** shows no distinct perturbation by the bornane moiety.

Barriers of such heights are very unusual<sup>13</sup> for open-shell tetrahedra. When diastereomerization of **3** was performed in the presence of racemic ligand, the third possible, completely asymmetric ( $C_1$  in **7a**) diastereomer **7** was also observed<sup>12,14</sup> as *RRS* (and/or its antipode<sup>2</sup> *RSS*). Both **4** and **7** NMR signals appear with comparable rates but now somewhat faster than in the absence of free ligand. Since **7** can be formed from **3** only by ligand exchange, it is clear that substitution can be faster than configurational inversion. Some mechanistic features of these competing pathways will be published shortly.

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- (8) Structural assignments of these compounds were based on full spectroscopic characterization and correct elemental analyses.
- (9) Configurational assignments at nickel are arbitrary but in no way relevant for the conclusions drawn here.
- (10) Optically active **3** crystallized in pure form from ethyl acetate-ethanol: mp 187-189 °C; molecular mass (benzene) calcd 718, found 690; magnetic dipole moment, found 3.14  $\mu_B$  in (Cl<sub>2</sub>CD)<sub>2</sub> at 26 °C.
- (11) Knorr, R.; Polzer, H.; Bischler, E. *J. Am. Chem. Soc.* **1975**, *97*, 643-644.
- (12) The reduced NMR shifts<sup>11</sup> of these 4-H's are  $\delta$  +25.7 and +29.3 ppm for **3**, +27.0 and +28.3 ppm for **4**, +26.4 and +30.5 ppm for **7**.
- (13) See ref 2 and 5 for some relevant references.
- (14) The resultant mixture showed the same NMR shifts as a solution of the nickel complex<sup>9</sup> (mp 237.5-239 °C) prepared from the racemic ligand.

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## Time-Resolved CIDEP and ESR Studies of Heavy Metal–Organic Radical Complexes. The Uranyl–Phenanthroquinone Radical Ions

Sir:

The rather turbulent debate as to the origins of the CIDEP (chemically induced dynamic electron polarization) observed in the ESR spectra of photogenerated radicals has abated, and, as it is now generally accepted that there are two distinctly different mechanisms,<sup>1</sup> interest has turned to chemical applications. While almost all of the CIDEP initial polarization systems reported to date involve the photochemical triplet of organic carbonyl compounds,<sup>1</sup> our recent efforts in CIDEP applications have been mainly directed towards metal–quinone complexes, particularly the *o*-phenanthroquinone (PQ).<sup>2</sup> We report here our first successful application of time-resolved CIDEP to heavy metal–organic radical complexes: the uranyl–phenanthroquinone radical ions. Historically the photochemistry of uranyl ion has played an important role<sup>3</sup> in the development of modern photochemistry. The CIDEP results will shed some light on the primary photochemical processes of uranyl ions and the ESR characterization of the uranyl–quinone complex ions should be of wider interest to chemistry in general.

The laser flash photolysis (Molelectron 1-MW N<sub>2</sub> pulsed laser) and the time-resolved dc detection CIDEP observation system were assembled similarly to those reported by Kim and Weissman.<sup>4</sup> The total spectrometer dc response time was measured and found to be 0.2  $\mu$ s. A detailed examination of the system performance and the analysis of the relaxation measurements will be described elsewhere.

When a degassed THF containing 10<sup>-3</sup> M each of PQ and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was exposed briefly to light in the ESR cavity with 100-kHz modulation at -60 °C, a well-resolved spectrum was observed (Figure 1A). Prolonged UV irradiation led to the disappearance of the spectrum and in its place a new spectrum (Figure 1B) was developed when irradiation was terminated. Both spectra are characterized by a distinctly low *g* factor and their ESR parameters are given in Table I. The analyses of the hyperfine structures are consistent with the assignments of [UO<sub>2</sub>PQ]<sup>•+</sup> and [UO<sub>2</sub>HPQ]<sup>2•+</sup>, respectively, in which the unpaired spin is associated mainly with the phenanthroquinone moiety. The low *g* factor can be explained by the coordination to the uranium nucleus having a large spin-orbit coupling. Hyperfine interaction due to <sup>235</sup>U ( $I = 7/2$ ,

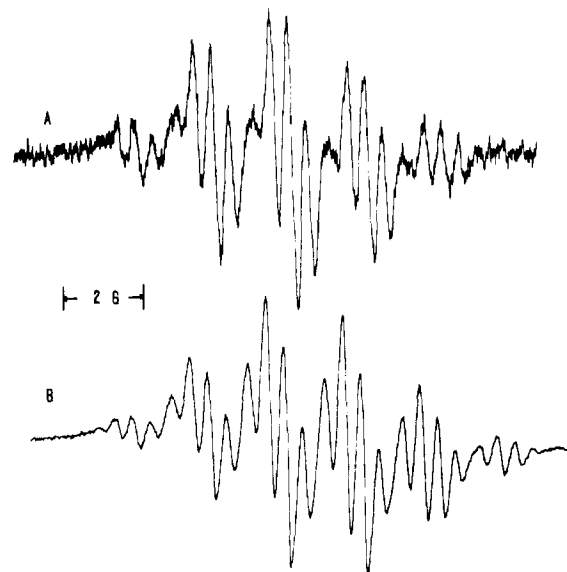


Figure 1. ESR spectra of (A) [UO<sub>2</sub>PQ]<sup>•+</sup> in THF at -60 °C, (B) [UO<sub>2</sub>HPQ]<sup>2•+</sup> in THF at -60 °C.

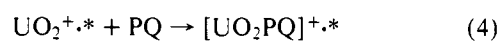
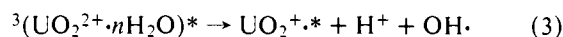
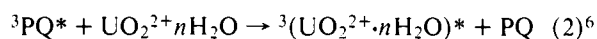
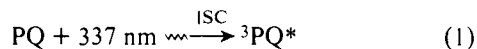
**Table I.** ESR Parameters<sup>a</sup> of Various Phenanthraquinone Complex Radicals in THF

complex	<i>T</i> , °C	<i>g</i>	<i>a</i> <sub>H</sub> , <sup>b</sup> G	<i>a</i> <sub>H(1,1')</sub>	<i>a</i> <sub>H(2,2')</sub>	<i>a</i> <sub>H(3,3')</sub>	<i>a</i> <sub>H(4,4')</sub>
[UO <sub>2</sub> PQ] <sup>+</sup>	-60	1.9940 ± 0.0001		1.86	0.43	1.86	0.43
[UO <sub>2</sub> HPQ] <sup>2+</sup>	-60	1.9945	1.43	1.86	0.43	1.86	0.43
PQ <sup>-</sup>	20	2.0045		1.54	0.32	1.70	0.41
K <sup>+</sup> PQ <sup>-</sup>	20	2.0046		1.43	0.26	1.68	0.44
CH <sub>3</sub> Hg-PQ	20	2.0005	0.16 (methyl)	1.69	0.41	1.85	0.41

<sup>a</sup> The numbering of protons follows the same convention as in ref 5. <sup>b</sup> The extra proton in [UO<sub>2</sub>HPQ]<sup>2+</sup> is assumed to be placed between the two carbonyl oxygens.

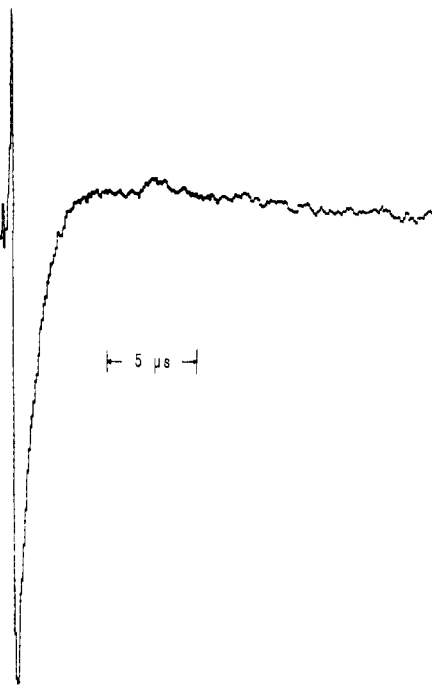
natural abundance 0.71%) was not resolved. The assignment of the primary [UO<sub>2</sub>PQ]<sup>+</sup> radical ion was further supported by a separate ion-exchange experiment<sup>5</sup> in which the K<sup>+</sup>PQ<sup>-</sup> ion pair was first prepared in THF by metal reduction. Upon addition of uranyl ions via a side-arm arrangement exchange took place and the resulting [UO<sub>2</sub>PQ]<sup>+</sup> (or the ion pair UO<sub>2</sub><sup>2+</sup>PQ<sup>-</sup>) gave a spectrum identical with that in Figure 1A.

Time-resolved CIDEP studies in the laser flash photolysis reveal a large initial polarization in [UO<sub>2</sub>PQ]<sup>+</sup> but not in the secondary [UO<sub>2</sub>HPQ]<sup>2+</sup> ion. A typical transient response at -60 °C from the laser generated [UO<sub>2</sub>PQ]<sup>+</sup> ion is shown in Figure 2. In the absence of uranyl ions, neither thermalized nor polarized PQ<sup>-</sup> was observed. However, laser flash photolysis of a THF solution containing PQ and triethylamine yields a strongly polarized PQ<sup>-</sup> exhibiting both initial and radical-pair polarizations. With the uranyl-PQ system both the uranyl ion and PQ absorb at the laser wavelength of 337 nm. However, in the experiment the absorption by PQ at 337 nm is approximately two orders of magnitude larger than the uranyl ion. The initial polarization can thus be accounted for by the mechanism shown in eq 1-4 where \* denotes electron spin polarization. Reactions 3 and 4 can be regarded as a single step involving the spin-polarized triplet PQ reacting with UO<sub>2</sub><sup>2+</sup>·*n*H<sub>2</sub>O to form [UO<sub>2</sub>PQ]<sup>+</sup>. Subsequent experiments using traces of added acid or base indicate, however, that the stepwise mechanism is more appropriate.

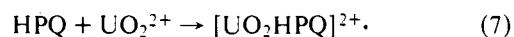
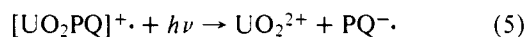


From the analysis of the transient response of the polarized [UO<sub>2</sub>PQ]<sup>+</sup> radical ion, an estimated *T*<sub>1</sub> of <0.8 μs is obtained. To date all of the quinone radical anions or semiquinone radicals, including the PQ<sup>-</sup> itself in amine, have *T*<sub>1</sub> values between 4 and 10 μs (as measured by time-resolved CIDEP in our laboratory) which are in good agreement with those values reported by McLauchlan and co-workers.<sup>7</sup> This significant reduction in *T*<sub>1</sub> in [UO<sub>2</sub>PQ]<sup>+</sup> can be considered as a further evidence of complexation of PQ<sup>-</sup> to UO<sub>2</sub><sup>2+</sup> in which the large spin orbit interaction as indicated by the low *g* factor provides an additional relaxation mechanism.<sup>8</sup>

The secondary photochemical reaction leading to the formation of an unpolarized radical ion [UO<sub>2</sub>HPQ]<sup>2+</sup> is of some interest to the potential application of uranyl ions as water-splitting photosensitizers. It has been established by using THF-*d*<sub>8</sub> as solvent that the extra proton does not come from solvent and thus reaction 3 is probably the source of the proton. Furthermore, addition of a trace of base such as NaOH suppresses the formation of [UO<sub>2</sub>HPQ]<sup>2+</sup>, while the addition of acid seems to facilitate its formation. CIDEP results also suggest that the formation of [UO<sub>2</sub>HPQ]<sup>2+</sup> is mainly a secondary photochemical reaction. A reasonable reaction mechanism to account for the formation of [UO<sub>2</sub>HPQ]<sup>2+</sup> is proposed:



**Figure 2.** Transient emissive response from laser generated [UO<sub>2</sub>PQ]<sup>+</sup> at -60 °C. *B*<sub>1</sub> is ~40 mG. The curve represents the difference between the on resonance and off-resonance responses.



In a light modulation experiment, the presence of PQ<sup>-</sup> (*g* = 2.0045) was confirmed by ESR. Direct observation of the radical HPQ, however, was not possible under the experimental conditions and this may be due to the rapid association of HPQ with the uranyl ions in reaction 7. Similar results have been obtained with other *o*-quinones such as the *o*-naphthaquinone. Further investigation of the uranyl photochemical reactions with various ketones, quinones, and other organic substrates is in progress.

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McGlynn and Smith (S. P. McGlynn and J. K. Smith, *J. Mol. Spectrosc.*, **6**, 164 (1961)) have suggested that the lowest absorption between 20 500 and 30 000  $\text{cm}^{-1}$  results from a singlet-triplet transition. They also noted that the excited uranyl complex is weakly paramagnetic.

- (7) For example, see K. A. McLaughlin, R. C. Sealy, and J. M. Wittman, *Mol. Phys.*, **36**, 1397 (1978), and references therein.  
 (8) We thank a referee who reminded us that the large spin orbit interaction is probably responsible for the fast relaxation.

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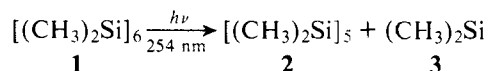
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## Dimethylsilylene, $(\text{CH}_3)_2\text{Si}$

Sir:

Dimethylsilylene,  $(\text{CH}_3)_2\text{Si}$ , has been frequently postulated as an organosilicon reaction intermediate<sup>1</sup> but has never been observed. We now report the preparation and spectroscopic characterization of this elusive species in hydrocarbon glasses and inert gas matrices at low temperatures. It is noteworthy that dimethylsilylene is stable indefinitely in hydrocarbon glasses at 77 K, permitting its use as a preformed reagent.

Irradiation of solutions of dodecamethylcyclohexasilane (**1**) is well known to produce decamethylcyclopentasilane (**2**). The  $(\text{CH}_3)_2\text{Si}$  residue appears as a polymer,  $[(\text{CH}_3)_2\text{Si}]_n$ , or can be transferred to suitable trapping agents.<sup>2</sup> We find that irradiation of **1** in rigid hydrocarbon glasses (3-methylpentane (3-MP), methylcyclohexane, or decalin) at 77 K or in an argon matrix at 10 K produces **2**, characterized by comparison of its UV and IR spectra with those of an authentic sample, and a new bright yellow species (**3**).



In 3-methylpentane glass **3** shows a broad electronic absorption band at 453 nm ( $\epsilon \approx 1500$ ) and a weak fluorescence peaking at 655 nm, depicted in Figure 1. In argon matrix, the absorption peak is shifted to 445 nm. The fluorescence excitation spectrum follows the shape of the absorption band. A characteristic infrared absorption is found for **3** at 1220  $\text{cm}^{-1}$ , in a region free of absorption by **1** and **2**. The visible and infrared absorptions both disappear when the glass or matrix is warmed to its softening point.

The spectroscopic data are compatible with assignment of **3** as  $(\text{CH}_3)_2\text{Si}$ . The electronic absorption band for **3** lies near those for  $\text{SiH}_2$  (480–650 nm)<sup>3a</sup> and  $\text{SiHCl}$  (500 nm),<sup>3b</sup> and the infrared band may be assigned to a methyl symmetrical deformation vibration.<sup>4a</sup>

Convincing evidence for the identification of **3** as  $(\text{CH}_3)_2\text{Si}$

is provided by the results of chemical trapping experiments. Trapping agents used were triethylsilane (**4**), bis(trimethylsilyl)ethyne (**5**), and 1-hexene (**6**). Typically, 0.3 mL of trapping agent and 6 mg of **1** were dissolved in 1.7 mL of 3-MP, cooled to 77 K, and irradiated for  $\sim 10$  min at 254 nm, producing the deep yellow color of **3**. When the mixture was warmed to melt the matrix, the color disappeared. The procedure was repeated several times until irradiation no longer produced a yellow color. The expected<sup>2a</sup> product from **4**, 1,1,1-triethyl-2,2-dimethyldisilane (**7**), was isolated by preparative GC and identified by its <sup>1</sup>H NMR and mass spectra. The initial product from the reaction of **5** with **3** was treated with methanol, yielding 1,2-bis(trimethylsilyl)vinyl dimethylmethoxysilane,<sup>5</sup> identified by GC-mass spectrometry. The initial product from the reaction of **6** with **3** was treated with ethanol, yielding hexyldimethylethoxysilane,<sup>6</sup> again identified by GC-MS. These are the products expected<sup>7</sup> from alcoholysis of the primary adducts of dimethylsilylene to the multiple bonds. Yields in all three reactions were  $\sim 60\%$  (by GC).

In the absence of a trapping agent,  $[(\text{CH}_3)_2\text{Si}]_n$  polymer was formed when the hydrocarbon matrix containing **3** was melted. The same result was obtained when dimethyldimethoxysilane was present as a potential trapping agent. The fact that little or no 1,2-dimethoxytetramethyldisilane was produced is of interest, because dimethyldimethoxysilane is believed<sup>2a</sup> to trap efficiently dimethylsilylene photogenerated in lower concentrations in fluid solutions at higher temperatures.

Significantly, when the irradiation of **1** is performed in 2-methyltetrahydrofuran glass at 77 K, conversion into **2** is observed in the UV spectrum, but the absorption band of **3** does not appear and the glass remains colorless. We believe that **3** is still generated but reacts with the solvent. In the presence of the trapping agent, **4**, we detect only a few percent of the trapping adduct **7**, in contrast to the 60% formed in a hydrocarbon solvent under otherwise similar conditions. This result confirms our assignment of the yellow species as the one which is being trapped in hydrocarbon solvents, i.e., as **3**.

The rigid solutions of **3** have no ESR signal, indicating that **3** is a ground-state singlet, similar to known inorganic silylenes.<sup>3,8</sup> The huge Stokes shift between the maxima for the absorption and fluorescence bands (Figure 1) suggests a large change of geometry upon excitation, presumably a large increase of the C–Si–C angle. This difference is analogous to that established for inorganic silylenes.<sup>3</sup>

Irradiation of the rigid solutions of **3** with visible light slowly bleached the yellow color and caused the disappearance of the visible and IR absorption bands attributed to **3**. A new electronic absorption appeared at 260 nm, and several new IR bands emerged. One of these, at 2186  $\text{cm}^{-1}$ , is attributable to a Si–H stretching mode.<sup>4b</sup> Its appearance and position, which is high for a simple alkylsilane, are particularly significant and suggest that the photochemical process is a 1,2-hydrogen shift leading to 2-silapropene. This interesting transformation is

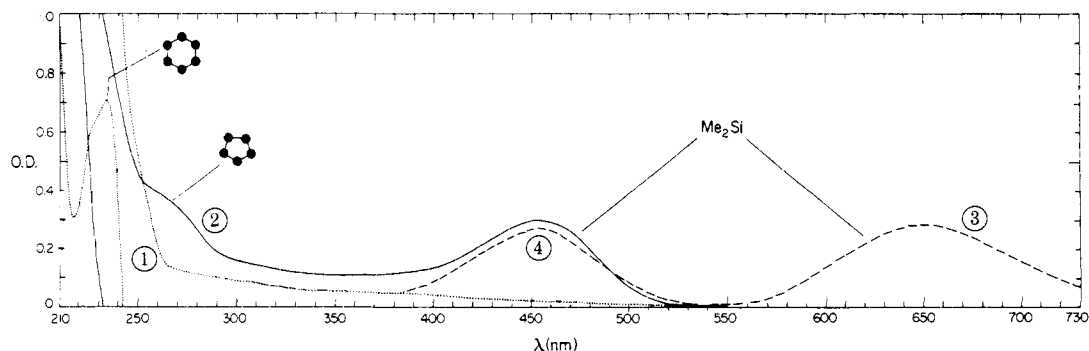


Figure 1. Absorption spectrum of **1** (1). Absorption (2), fluorescence (3), and excitation (4) spectra of a mixture of **2** and **3** obtained from **1** by UV irradiation (2 min), 77 K, 3-MP. Attribution of structural formulas to spectral bands is shown (a dark dot stands for the  $(\text{CH}_3)_2\text{Si}$  unit).