

Preparation and Structural Features of a Selenium Ylide, Diacetylmethylenediphenylselenurane

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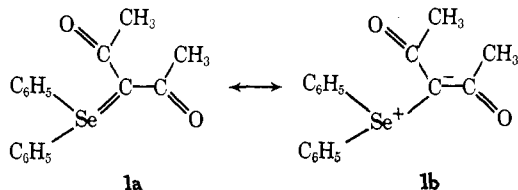
Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801, and the Belfer Graduate School of Science, Yeshiva University, New York, New York 10033. Received February 27, 1974

Abstract: Diacetylmethylenediphenylselenurane, **1**, a selenium ylide, was prepared by the reaction of diphenylselenium dichloride with sodium acetylacetonate in methanol solution. The nmr spectrum showed a methyl singlet at δ 2.43 ppm. X-Ray analysis confirmed the structure as an ylide and showed that the configuration at selenium was pyramidal with Se lying 0.78 Å out of the plane of its three bonded atoms. Low-temperature nmr studies show that the equilibration of the two methyl groups proceeds *via* an energy barrier of <10 kcal/mol. The crystals of **1** are monoclinic with $a = 13.297$ (7), $b = 13.418$ (6), $c = 9.112$ (5) Å, and $\beta = 111.7$ (1)°; the space group is $P2_1/c$ and there are four molecules of $C_{17}H_{16}O_2Se$ in the unit cell.

Sulfonium ylides have been the subject of extensive investigation with several of them having been isolated and their properties investigated.³⁻¹⁸ Recently Lloyd and coworkers have prepared a series of heteronium tetraphenylcyclopentadienyliides of groups V and VI including those of selenium and tellurium.^{14,15} In view of the interest of such compounds we have prepared a noncyclic selenium ylide (selenurane(IV)),¹⁶ and we wish to report its synthesis, spectral properties, and structural data derived from X-ray diffraction results.

Results and Discussion

The crystalline diacetylmethylenediphenylselenurane, **1**, was prepared from diphenylselenium dichloride and **2**



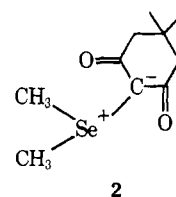
equiv of sodium acetylacetonate in methanol solution at room temperature. The requirement of a second mole

- (1) University of Illinois.
- (2) Yeshiva University.
- (3) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).
- (4) E. D. Hughes and K. I. Kuriyan, *J. Chem. Soc.*, 1609 (1935).
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- (9) (a) H. Nozaki, K. Kondo, and M. Takau, *Tetrahedron Lett.*, 251 (1965); (b) Y. Hayasi and H. Nozaki, *Tetrahedron*, **27**, 3085 (1971); (c) H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *ibid.*, **23**, 4279 (1967).
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- (14) (a) D. Lloyd and M. I. C. Singer, *Chem. Commun.*, 390 (1967); (b) B. H. Freeman and D. Lloyd, *ibid.*, 924 (1970); (c) B. H. Freeman, D. Lloyd, and M. I. C. Singer, *Tetrahedron*, **28**, 343 (1972).
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of sodium acetylacetonate in the reaction indicates that the reaction may proceed through the nucleophilic displacement of chlorine on selenium by acetylacetonate anion, followed by proton abstraction of diacetylmethylenediphenylselenium chloride with another mole of sodium acetylacetonate. The selenurane **1** was stable upon standing in the atmosphere. The stability of the selenurane **1** is enhanced due to the delocalization afforded the carbanion by the carbonyl groups. The carbonyl groups of the selenurane gave a broad ir absorption at 1520 cm^{-1} . The nmr spectrum shows a methyl singlet and an aromatic multiplet. Cooling to -60° led to no detectable broadening of the methyl peak. The mass spectrum of **1** shows the largest molecular peak at m/e 332 in greatest abundance thus indicating the high stability of the molecular ion. Significant fragments were observed at m/e 234 which corresponds to $(C_6H_5)_2Se^+$, at m/e 157 which corresponds to $C_6H_5Se^+$, at m/e 154 which corresponds to $(C_6H_5)_2^+$, and at m/e 77 which corresponds to $C_6H_5^+$. The loss of one methyl group at m/e 317 is also observed.

Final proof of structure and the determination of molecular geometry was achieved by X-ray structure analysis. The orange crystals of **1** are monoclinic with $a = 13.297$ (7), $b = 13.418$ (6), $c = 9.112$ (5) Å, and $\beta = 111.7$ (1)°. There are four molecules of $C_{17}H_{16}O_2Se$ in the unit cell and the space group is $P2_1/c$. A stereoscopic view of a single molecule of **1** is shown in Figure 1. Bond lengths and angles are listed in Table I.

When this work was complete, two recent papers on selenium ylides from the Russian literature came to our attention.^{17,18} In one of these,¹⁷ the structure of the selenium ylide **2** was reported. In the other paper,¹⁸



- (17) V. V. Saatsazov, R. A. Kyandzhetsian, S. I. Kuznetsov, N. N. Madgesieva, and T. C. Khotsyanova, *Dokl. Akad. Nauk. SSSR*, **206**, 1130 (1972).
- (18) V. V. Saatsazov, R. A. Kyandzhetsian, S. I. Kuznetsov, N. N. Madgesieva, and T. C. Khotsyanova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 671 (1973).

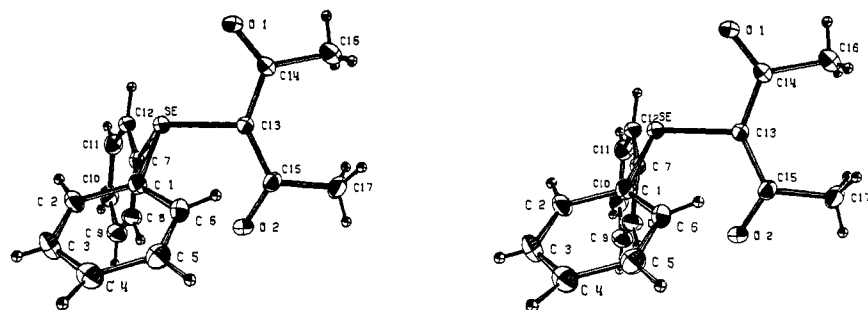


Figure 1. Stereoscopic view of a molecule of **1**.

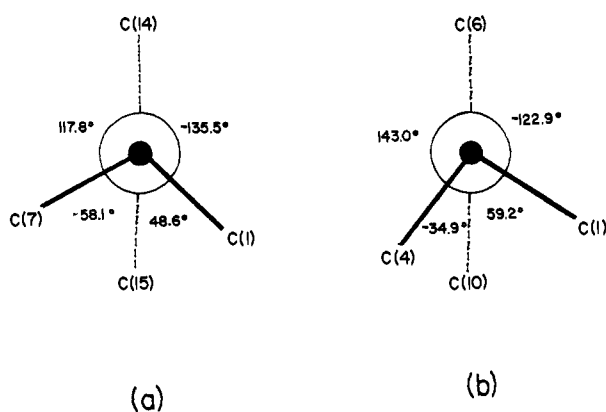


Figure 2. Projections down the Se-C(acetylacetonate) bond (a) in **1** and (b) in **2**. The torsion angles are defined as positive if the atom bonded to Se has to be rotated clockwise to eclipse the atom attached to C.

Table I. Bond Lengths and Angles in **1**^a

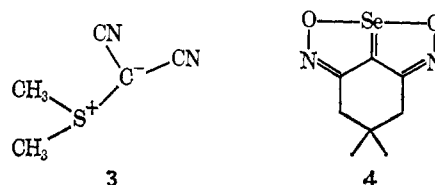
Bond Lengths, Å			
Se-C(1)	1.898 (9)	C(9)-C(10)	1.363 (16)
Se-C(7)	1.926 (9)	C(10)-C(11)	1.374 (15)
Se-C(13)	1.906 (8)	C(11)-C(12)	1.381 (15)
C(1)-C(2)	1.394 (12)	C(7)-C(12)	1.376 (12)
C(2)-C(3)	1.367 (15)	C(13)-C(14)	1.420 (11)
C(3)-C(4)	1.373 (16)	C(13)-C(15)	1.441 (11)
C(4)-C(5)	1.393 (14)	C(14)-C(16)	1.523 (16)
C(5)-C(6)	1.371 (13)	C(14)-O(1)	1.222 (11)
C(1)-C(6)	1.395 (12)	C(15)-C(17)	1.503 (16)
C(7)-C(8)	1.388 (11)	C(15)-O(2)	1.219 (10)
C(8)-C(9)	1.386 (15)		
Bond Angles, deg			
C(1)-Se-C(7)	100.8 (3)	C(7)-C(8)-C(9)	118.9 (9)
C(1)-Se-C(13)	107.5 (3)	C(8)-C(9)-C(10)	120.3 (10)
C(7)-Se-C(13)	105.0 (3)	C(9)-C(10)-C(11)	120.5 (10)
Se-C(1)-C(2)	119.0 (6)	C(10)-C(11)-C(12)	120.2 (10)
Se-C(1)-C(6)	122.0 (6)	C(7)-C(12)-C(11)	119.3 (8)
C(2)-C(1)-C(6)	118.5 (8)	Se-C(13)-C(14)	109.3 (6)
C(1)-C(2)-C(3)	120.3 (9)	Se-C(13)-C(15)	116.4 (6)
C(2)-C(3)-C(4)	121.7 (10)	C(14)-C(13)-C(15)	134.1 (8)
C(3)-C(4)-C(5)	118.3 (10)	C(13)-C(14)-C(16)	120.8 (9)
C(4)-C(5)-C(6)	121.0 (9)	C(13)-C(14)-O(1)	121.5 (8)
C(1)-C(6)-C(5)	120.2 (8)	C(16)-C(14)-O(1)	117.5 (9)
Se-C(7)-C(8)	124.7 (6)	C(13)-C(15)-C(17)	120.7 (8)
Se-C(7)-C(12)	114.6 (6)	C(13)-C(15)-O(2)	121.5 (8)
C(8)-C(7)-C(12)	120.7 (8)	C(17)-C(15)-O(2)	117.8 (8)

^a Estimated standard deviations in parentheses.

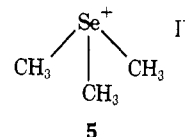
some crystal data on a series of selenium ylides were reported but no structural results had yet been obtained.

The configuration at selenium in **1** is seen to be pyramidal with Se lying 0.78 Å out of the plane of its three bonded atoms. The Se-C(13) bond is 1.906 (8)

Å, and the Se-C(phenyl) lengths are 1.898 (9) and 1.926 (9) Å. The configuration at selenium and the long Se-C(13) bond are indicative of a large contribution from the ylide resonance structure **1b**. X-Ray data on a sulfur ylide **3** revealed that the sulfur atom lay



0.74 Å out of the plane of its three neighbors,¹⁹ while the selenium-containing compound **4** had an effectively planar arrangement at selenium and an Se-C distance of 1.802 (11) Å, a value which implied considerable double bond character in the Se-C bond in **4**.²⁰ In **2**, the two Se-C bonds in the five-membered ring were much longer (1.99 and 2.01 Å) than in **1** and the selenium lay even further (0.91 Å) out of the plane of its three bonded neighbors. In the salt, trimethylselenonium iodide, **5**, the selenium lay 0.95 Å out of the



plane of its three bonded neighbors.^{21a} We have recently prepared what we believe to be the first tetra-valent five-coordinate compound of selenium(IV) from an acetylacetonate of triphenylselenium.^{21b} The bond angles around Se in **1** are C(1)-Se-C(7) 100.8 (3)°, C(1)-Se-C(13) 107.5 (3)°, and C(7)-Se-C(13) 105.0 (3)°. The C(1)-Se-C(7) bond angle of 100.8 (3)° is quite close to those found in **5**, 97.9 (7) and 99.1 (7)°,²¹ and in dimethylselenium, 98°.²² It is significantly smaller than the values found in di-*p*-tolylselenium (106 (2)°)²³ or in its dibromo or dichloro substituents (106.5 (1.0) and 108 (1)°,²⁴ respectively) but clearly larger than the 90° found in **2**.

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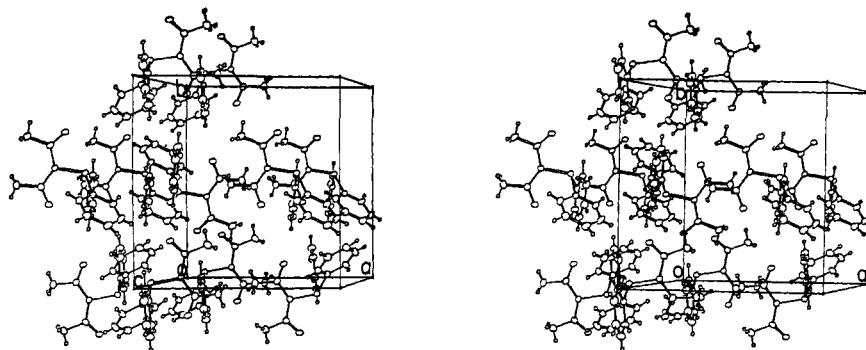


Figure 3. Stereoscopic view of the contents of the unit cell for **1**. The reference molecule has heavily shaded bonds.

In the crystal, the molecule of **1** does not have exact C_s symmetry through the plane containing the selenium atom and the acetylacetonate moiety. The orientation of the two phenyl rings is quite different with respect to this plane. As can be appreciated from Figure 2, the projection angles down the Se–C(13) bond are also unsymmetrical. A somewhat similar unsymmetrical projection down the Se–C(acetylacetonate) bond was noted in the structure of **2** (see Figure 2b).

The packing in the crystal is shown in Figure 3. There is no evidence for significant intermolecular interaction involving selenium. The closest contact is of 3.65 Å to C(4) in the molecule at $-x, 1-y, 1-z$. The mode of packing is strongly suggestive of a molecular crystal and does not indicate any significant ionic interactions.

The spectroscopic properties of **1** can be interpreted in terms of the molecular structure. A broadening observed in the ir results from the presence of two distinguishable carbonyl groups. A similar broadening in the ir also appears in a sulfonium ylide.^{9a} The lack of broadening of the methyl peak in the nmr upon cooling to -60° indicates that the equilibration of the two methyls proceeds *via* an energy barrier of <10 kcal/mol. This behavior contrasts with that of the sulfonium ylide $(\text{CH}_3)_2\text{SC}(\text{COCH}_3)_2$ whose C-methyl signals broaden at -25° indicating a barrier of 12 kcal/mol, while other sulfonium ylides have still higher barriers.^{9c} Equilibration of the methyls can take place either *via* rotation about the Se–C bond or *via* inversion of the pyramid about the Se atom. The nonrearranging character of both sulfoxides and sulfonium ions,^{25a} and the expected low barrier to rotation in **1**, whether described as **1a** or **1b**, would favor the first of these alternatives. In principle, rotation about the $=\text{C}-\text{C}$ axis is also possible. However, it is not likely, and there is no obvious way to demonstrate it.

It is expected that when one or both of the carbonyls are replaced by another substituent incapable of allowing delocalization in the carbanion of **1**, compounds that could be useful in organic synthesis would be obtained. It should be noted that, in contrast to phosphonium ylides, the sulfonium and selenonium ylides could, in principle, be converted to S(VI) and Se(VI) compounds such as $(\text{C}_6\text{H}_5)_2\text{Se}[\text{C}(\text{COCH}_3)_2]\text{O}$ and $(\text{C}_6-$

Table II. Final Atomic Coordinates for **1** in Fractions of Unit Cell Edge^a

	<i>x</i>	<i>y</i>	<i>z</i>
Se	0.18139 (6)	0.45366 (5)	0.85496 (10)
C(1)	0.1028 (6)	0.5557 (5)	0.7153 (9)
C(2)	0.0143 (7)	0.5987 (6)	0.7381 (11)
C(3)	-0.0497 (8)	0.6657 (8)	0.6313 (13)
C(4)	-0.0308 (8)	0.6912 (7)	0.4978 (12)
C(5)	0.0562 (8)	0.6470 (7)	0.4727 (11)
C(6)	0.1222 (7)	0.5804 (7)	0.5793 (10)
C(7)	0.2268 (6)	0.5229 (5)	1.0540 (9)
C(8)	0.2413 (8)	0.6253 (6)	1.0718 (11)
C(9)	0.2772 (9)	0.6655 (7)	1.2226 (13)
C(10)	0.2990 (8)	0.6051 (8)	1.3509 (12)
C(11)	0.2839 (8)	0.5039 (8)	1.3326 (12)
C(12)	0.2471 (7)	0.4622 (5)	1.1835 (11)
C(13)	0.3110 (6)	0.4314 (5)	0.8163 (10)
C(14)	0.3282 (7)	0.3273 (6)	0.8104 (11)
C(15)	0.3726 (7)	0.5186 (6)	0.8104 (10)
C(16)	0.4295 (10)	0.2874 (8)	0.7901 (23)
C(17)	0.4752 (8)	0.5094 (8)	0.7783 (15)
O(1)	0.2663 (6)	0.2665 (4)	0.8313 (10)
O(2)	0.3452 (5)	0.6017 (4)	0.8349 (7)
H(2)	0.017 (8)	0.572 (7)	0.836 (12)
H(3)	-0.094 (8)	0.686 (8)	0.650 (13)
H(4)	-0.091 (7)	0.727 (6)	0.401 (10)
H(5)	0.071 (6)	0.666 (6)	0.383 (10)
H(6)	0.174 (7)	0.551 (6)	0.574 (10)
H(8)	0.231 (6)	0.658 (5)	0.989 (9)
H(9)	0.282 (7)	0.724 (6)	1.220 (10)
H(10)	0.323 (6)	0.637 (6)	1.448 (9)
H(11)	0.291 (9)	0.472 (8)	1.401 (14)
H(12) ^b	0.238	0.393	1.167
H(16a)	0.420	0.299	0.691
H(16b)	0.496	0.298	0.898
H(16c)	0.425	0.223	0.819
H(17a)	0.463 (8)	0.470 (7)	0.682 (12)
H(17b)	0.528 (7)	0.473 (6)	0.863 (10)
H(17c)	0.494	0.564	0.765

^a Standard deviations given in parentheses. ^b Hydrogen atoms for which standard deviations are not given were held at fixed positions, found from the difference map.

$\text{H}_5)_2\text{Se}[\text{C}(\text{COCH}_3)_2]_2$ increasing the valence by two and reorganizing the geometry. It should be noted that the C–S–C bond angle for a sulfur(IV) oxide is 117.7° ,^{25b} as compared with the values of 104.4 and 107.8° for unsubstituted sulfuranes.^{25b,c} The expansion here is due to the role of the s electrons in the oxide.^{25b,c}

Experimental Section

The melting point is uncorrected. The infrared spectrum was obtained using Perkin-Elmer Model 467 spectrophotometer. The nmr spectrum was recorded with a Varian A-60A spectrometer at ambient temperature and at -60° . Chemical shifts are given in parts per million downfield from TMS internal standard. The mass spectrum was recorded using a Du Pont 21-492 mass spectrom-

(25) (a) C. A. Maryanoff, B. E. Maryanoff, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 5839 (1973); (b) E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Amer. Chem. Soc.*, **96**, 578 (1974); *ibid.*, submitted for publication; (c) I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **94**, 5010 (1972).

eter at 70 eV. Microanalysis was performed by Galbraith Laboratory, Knoxville, Tenn.

Preparation. A solution of diphenylselenium dichloride (1.52 g, 0.0050 mol) in 35 ml of spectrograde methanol was treated with a solution of sodium acetylacetonate (1.25 g, 0.0102 mol) in 15 ml of methanol at room temperature. Instant color change of solution from yellow to orange was observed. After being stirred for 3 hr the solvent was removed and the remaining solids were extracted with chloroform and filtered to remove unreacted materials and sodium chloride. Addition of petroleum ether to the filtrate and cooling the solution gave the crude product. Recrystallization of the crude product from chloroform-petroleum ether gave 0.98 g (60% yield) of light orange crystals of diacetylmethylenediphenylselenurane, **1**; mp 125–126.5°; ir (KBr pellet) 3035 (m), 2960 (m), 1950 (w), 1560 (s, shoulder), 1520 (s, broad), 1450 (m), 1428 (m), 1400 (m), 1350 (s), 1320 (s), 1300 (s), 1270 (s), 1175 (m), 1060 (m), 1010 (m), 990 (m), 930 (s), 838 (w), 740 (s), 685 (s), 600 (s), 585 (s), 450 (s), 325 (m), 305 (m); ¹H nmr (CDCl₃) δ 2.43 (s, 6 H), 7.41–7.65 (m, 10 H); mass spectrum *m/e* 332 (M⁺), 317 (M⁺ – CH₃), 290, 239, 234 (Ph₂Se⁺), 223, 211, 195, 175, 157 (C₆H₅Se⁺), 154 ((C₆H₅)₂Se⁺), 132, 117, 94, 77 (C₆H₅⁺).

Anal. Calcd for C₁₇H₁₆O₂Se: C, 61.63; H, 4.86. Found: C, 62.02; H, 4.83.

X-Ray Analysis. A small crystal 0.10 × 0.20 × 0.15 mm was mounted along the *b* axis (0.20 mm). Cell data (from a least-squares fit to the settings for 12 reflections, Cu Kα, λ 1.54178 Å) are C₁₇H₁₆O₂Se, mol wt = 335.25, monoclinic, *a* = 13.297 (7), *b* = 13.418 (6), *c* = 9.112 (5) Å, β = 111.7 (1)°; *V* = 1510 × 10⁻²⁴ cm³, *Z* = 4, *D*_{calcd} = 1.475 g cm⁻³, μ = 37.6 cm⁻¹ (Cu Kα), space group *P*2₁/*c*.

Intensity data were collected as described previously.^{26,27} A total of 2680 intensities was measured, 2370 of which were considered above background at the 2σ level based on counting statistics. The structure was solved by the heavy-atom method. The model including positional and anisotropic thermal parameters

(26) J. K. Frank and I. C. Paul, *J. Amer. Chem. Soc.*, **95**, 2324 (1973).

(27) R. S. Miller, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, submitted for publication.

for the nonhydrogen atoms was refined to an *R* factor of 0.099 on all nonzero reflections. A difference map calculated at this stage in the analysis provided positions for all the hydrogen atoms. However, some of these atoms moved to rather unreasonable positions where they were included in the refinement process and were subsequently constrained at the positions found from the difference map. After convergence of the least-squares refinement, the final *R* factor on all nonzero reflections was 0.088. The list of atomic coordinates is given in Table II. The final thermal parameters and the observed and calculated structure factors will appear in the microfilm edition.²⁸ A weighting scheme based on that proposed by Corfield, Doedens, and Ibers²⁹ was used in the refinement. The scattering curves for Se, C, and O were from the compilation by Cromer and Mann,³⁰ that from hydrogen being the one calculated by Stewart, *et al.*³¹

Acknowledgment. The work (at the University of Illinois) was supported by the Hoffmann-La Roche Foundation and (at Yeshiva University) by the Office of Naval Research Contract N 00014-68-A-0302-0005.

Supplementary Material Available. The final thermal parameters and the values of *h*, *k*, *l*, |*F*_o|, and *F*_c for **1** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4099.

(28) See paragraph at end of paper regarding supplementary material.

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(31) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Short-Wavelength, Ultraviolet Photolysis of Metal Complexes. Substantial Photoreduction of Ruthenium Complexes

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Contribution from the Department of Chemistry, Boston University, Boston, Massachusetts 02215. Received October 23, 1973

Abstract: Unlike previous investigations at 185 nm which have been characterized by the photolysis of water and not the solute, this report centers upon the solute (the metal complexes) absorbing most of the light at 185 nm. Photolysis of Ru(NH₃)₆³⁺, Ru(NH₃)₅OH₂³⁺, and Ru(NH₃)₅Cl²⁺ at 185 nm has been investigated. Substantial photoreduction (Φ_r ~ 0.65) of Ru(NH₃)₆³⁺ was observed in the presence of small amounts of 2-propanol, methanol, or ethanol. Photolysis at 254, 229, and 214, while resulting in some photoreduction, gave no apparent indication of the enhanced photoreduction observed at the higher energy. The rapid rise in Φ_r in the low uv corresponds to the onset of the charge-transfer band of the ruthenium complex. On the contrary, photoaquation is not similarly enhanced on going from 254 to 185 nm. A mechanism is proposed in which the 2-propanol serves as a radical scavenger of photoexcited ruthenium radical. The 2-propanol radical which results (free or coordinated) undergoes hydrogen abstraction to produce a mole of acetone and 0.5 mol of hydrogen. (Φ_r = Φ_{acetone} = 2Φ_{H₂})

As compared with the large number of reports at 254 nm, low uv photolysis of metal complexes at 185 nm has received little attention.¹ It has readily been demonstrated that 254-nm photolysis of metal complexes can activate a molecule coordinated to a metal center.^{2,3} Recent investigators^{4,5} have con-

centrated on 229- and 214-nm irradiation of inorganic salts. In the past, photochemistry below 200 nm has

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