[Pt(bipy)(en)]I₂ d, A.	I/I₀	[Pt(bipy)(en-H)]I d, Å.	I/I₀	[Pt(bipy)(en-2H)] d, Å.	I/I₀
4.92	0.8	9.40	1.0	7.16	1.0
4.27	0.9	5.47	0.7	4.64	0.4
4.06	0.9	5.09	0.8	3.39	0.4
3.63	1.0	3.93	0.7	2.81	0.3
3.41	0.3a	3.63	0.7	2.46	0.2a
3.23	0.3	3.30	0.4	2.21	0.2
3.14	0.4	2.91	0.2a	2.02	0.2
2.53	0.5	2.49	0.2		

[Pt(bipy)(en-CH₃)]I₂·0.5H₂O d, Å.	I/I₀	[Pt(bipy)en(CH₃)₂]I₂ d, Å.	I/I₀
8.13	0.3a	5.13	0.7
6.87	0.3	4.27	1.0
5.91	0.3	4.00	0.2a
5.16	1.0	3.45	0.8
4.24	0.9	3.14	0.2
3.94	0.4	3.09	0.2
3.52	0.4	2.62	0.4
3.16	0.3	2.42	0.2

a Less intense lines not included here.

Anal. Calcd. for [Pt(bipy)(en)]I₂: Pt, 29.4; I, 38.2. Found: Pt, 29.2; I, 38.1.

By methods previously described,[4] bipyridyl-β-aminoethylamidoplatinum(II) iodide, [Pt(bipy)(en-H)]I, was prepared by treating [Pt(bipy)(en)]I₂ with 1 molar equiv. of KNH₂ in liquid ammonia at −35°. The solid product was filtered, washed thoroughly with liquid ammonia, and dried *in vacuo* at 25° for 16 hr. Thereafter this product was stored in a dry helium atmosphere.

Anal. Calcd. for [Pt(bipy)(en-H)]I: Pt, 36.3; I, 23.6; equiv. wt., 537. Found: Pt, 36.6; I, 23.4; equiv. wt., 540 (by HI titration).

Bipyridylethylenediamidoplatinum(II), [Pt(bipy)(en-2H)], was prepared by treating [Pt(bipy)(en)]I₂ with slightly more than 2 molar equiv. of KNH₂ in a manner analogous to that described above.

Anal. Calcd. for [Pt(bipy)(en-2H)]: Pt, 47.7; C, 35.2; H, 3.5; N, 13.7; equiv. wt., 205. Found: Pt, 47.4; C, 35.3; H, 3.6; N, 13.4; equiv. wt., 203.

Approximately 15 ml. of doubly distilled CH₃I was added to about 0.3 g. of [Pt(bipy)(en-H)]I in a tube containing a magnetic stirring bar. The tube was sealed and its contents stirred for 2 weeks at 25°. Thereafter, excess CH₃I was removed by distillation; the dark yellow residue was dried *in vacuo* for 3 hr. and recrystallized[5] from water.

Anal. Calcd. for [Pt(bipy)(en-CH₃)]I₂·0.5H₂O: Pt, 28.3; C, 22.7; N, 8.14; H, 2.78. Found: Pt, 28.2; C, 22.7; N, 8.46; H, 2.98.

The X-ray diffraction pattern (Table I) and infrared spectrum of this product were substantially identical with those of the authentic complex prepared from [Pt(bipy)Cl₂] and N-methylethylenediamine. Both spectra[6] included strong absorption bands at 722, 769, 1070, 1105, 1145, 1246, 1426, 1446, 1467, and 1606 cm.⁻¹.

A sample of [Pt(bipy)(en-2H)] was treated with excess CH₃I as described above to provide a greenish yellow solid after recrystallization.[7]

(4) G. W. Watt, *et al., J. Inorg. Nucl. Chem.*, **9**, 311 (1959); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 46, 454 (1955).

(5) During recrystallization, a relatively small but significant quantity of an as yet unidentified water-insoluble brown solid was separated.

(6) The interpretation of the spectra of these and related complexes will be given elsewhere.

Anal. Calcd. for [Pt(bipy)en(CH₃)₂]I₂: Pt, 28.2; C, 24.3; H, 2.90. Found: Pt, 28.1; C, 24.3; H, 3.06.

Both this product and the authentic complex prepared from [Pt(bipy)Cl₂] and N,N'-dimethylethylenediamine showed essentially identical X-ray diffraction patterns (Table I) and strong infrared absorption bands[6] at 724, 771, 850, 954, 1006, 1040, 1076, 1140, 1250, 1425, 1448, 1474, and 1604 cm.⁻¹.

Under conditions of methylation even more severe than those described above (90° in a sealed tube), [Pt(bipy)(en)]I₂ gave no evidence of reaction; the starting materials were recovered unchanged.

Because earlier efforts[8] to methylate [Pt(en-H)₂] were unsuccessful, the present results are significant not only *per se* but also because they demonstrate the effect of the bipy ligand upon the reactivity of the associated en. Study of this aspect of the problem and numerous other reactions of deprotonated ligands is in progress.

(7) In this case also a small quantity of a brown solid by-product was isolated.

(8) G. W. Watt and R. E. McCarley, unpublished results.

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Photosensitization of Ethylene with Mercury 6(¹P₁) Atoms[1]

Sir:

The mercury 6(³P₁) photosensitized reaction of ethylene has been studied extensively over the years in various laboratories and some excellent reviews have summarized all the pertinent past results.[2,3] The formation of electronically excited ethylene molecules in the primary process has become firmly established in the light of the past investigations.

In the present work photosensitization of ethylene has been carried out with Hg 6(¹P₁) atoms. This was accomplished with a new filter that absorbs the 2537-Å. resonance line and transmits the 1849-Å. resonance line, thus permitting only the production of the singlet excited mercury atoms in the reaction cell.[4] The reaction system consisted of an electrodeless mercury–argon discharge lamp made of a 8-mm. o.d. Suprasil tubing, which was excited by a microwave field and cooled by a flowing film of distilled water. Concentric and coaxial with the lamp was a filter cell, having a path length of about 1 mm. and a circulation system to prevent the filter solution from being heated. Concentric and coaxial with both the lamp and the filter cell was a reaction cell which had a path length of 7 mm. and was equipped with a cold finger. Owing to the damaging effect of oxygen on the dimethylanthracene filter, the solutions were made up under nitrogen atmosphere and provisions were made to prevent O₂ contamination during the reaction. All reactions were carried out with a −30° slush bath on the reaction cell cold finger trap, thus lowering the mercury vapor pres-

(1) This work was supported by a Contract with the U. S. Atomic Energy Commission [AT-(40-1)-2844].

(2) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd Ed., Reinhold Publishing Corp., New York, N. Y. 1954, p. 425.

(3) R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 84 (1964).

(4) C. M. Wolff and R. Pertel, *J. Opt. Soc. Am.*, **54**, 1168 (1964).

sure and assuring that the mercury resonance radiation will penetrate deeper into the reaction cell and therefore minimize any possible wall effects. Reaction products were analyzed by mass spectrometry, gas chromatography, and standard manometric methods. The reactions were run under static conditions at room temperature.

The major products found were hydrogen, acetylene, and n-butane. Ethane, propane, propylene, and n-butene-1 were determined in smaller amounts. The yields of the major products in 10-min. runs increased with the ethylene pressure up to about 60 to 70 torr. With further increase in total pressure the yields decreased. Assuming that the maximum corresponds to the onset of the complete quenching, we can estimate that the quenching cross section of ethylene with the Hg $6(^1P_1)$ atoms is about 20 to 25 times the value with the Hg $6(^3P_1)$ atoms (about 37 Å.^{2}), $i.e.$, about 740 to 925 Å.^{2}.

A mixture of equal amounts of C_2H_4 and C_2D_4 at a total pressure of 70 torr produced hydrogen in the following per cent ratio: $D_2:HD:H_2$ equal to 31.0: 2.7:66.3. The approximately 1:2 ratio of D_2 and H_2 is in keeping with similar isotope effects found with the Hg $6(^3P_1)$ atom reactions.[5] From the product and the hydrogen isotope analyses it can be concluded that intramolecular hydrogen molecule elimination takes place. Hydrogen atom elimination, if it occurs at all under these conditions, is a very minor process.

From the decrease of the product yield with increasing pressure one can conclude that in this case too we are dealing with an electronically excited ethylene molecule. The excited molecule then decomposes into hydrogen and acetylene molecules or is quenched by the other ground-state ethylene molecules, the latter process becoming more predominant as the pressure increases. In the case of the Hg $6(^3P_1)$ atom reactions it has been found that the isotopic composition of hydrogen from cis- and $trans$-dideuterioethylenes was identical.[6] In the case of the Hg $6(^1P_1)$ atom reactions we have found marked differences between cis and $trans$ isomers as well as when compared to the results of the triplet atom reactions in Table I.

Table I. Isotopic Composition of Hydrogen from cis- and $trans$-Dideuterioethylene Reactions

| | Hg $6(^1P_1)$ | | Hg $6(^3P_1)$ |
	cis	$trans$	cis and $trans$
H_2	33.1 ± 0.6	44.2 ± 2.0	23.1
HD	59.9 ± 0.5	48.9 ± 1.6	65.5
D_2	7.0 ± 0.2	6.8 ± 0.5	11.4

We can conclude from the data that the excited state of ethylene from which the decomposition takes place must be different from the state involved in the Hg $6(^3P_1)$ atom reactions. From recent spectroscopic evidence obtained by electron impact excitation it has been determined that ethylene has an excited triplet state ($^3B_{1u}$) at about 4.6 e.v. above the ground state and an excited singlet state at about 6.5 e.v. above the ground state.[7] The latter state has been ascribed to a transition analogous to the $\pi^* \leftarrow n$ transition in formaldehyde.[8]

(5) R. J. Cvetanović and A. B. Callear, *J. Chem. Phys.*, **23**, 1182 (1955).
(6) P. Ausloos and R. Gorden, *ibid.*, **36**, 5 (1962).
(7) A. Kupperman and L. M. Raff, *ibid.*, **37**, 2497 (1962).
(8) R. S. Berry, *ibid.*, **38**, 1934 (1963).

The excited mercury atoms in the triplet and singlet states correspond to 4.89 and 6.70 e.v., respectively, thus making it very natural to assume that they can produce the above-mentioned states of ethylene. The strong singlet–singlet transition resulting in the $^1B_{1u}$ state at about 7.7 e.v. is probably ruled out in the participation of the Hg $6(^1P_1)$ atom reaction, since it is generally recognized that the $^1B_{1u}$ and $^3B_{1u}$ states of ethylene have probably the same configurations, $i.e.$, the methylene groups twisted about 90° with respect to each other. This in turn would make it necessary that the isotopic composition of hydrogen from the cis- and $trans$-substituted dideuterioethylenes be the same. This was not observed in this study. It is conceivable, of course, that a collision complex between the excited mercury atoms and ethylene molecules is formed in the primary process. In that case we cannot make use of the spectroscopic states of ethylene in our discussion. Still the main conclusions remain unchanged: an excited "species" is produced in the primary process and it is different from the one produced by the Hg $6(^3P_1)$ atoms.

A more extensive paper about this reaction will be prepared in the near future from Mr. N. L. Ruland's Ph.D. thesis. This is the first of a contemplated series of papers about the Hg $6(^1P_1)$ atom reactions.

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Dimethyl Sulfoxide–Acid Anhydride Mixtures. New Reagents for Oxidation of Alcohols[1]

Sir:

We wish to report a novel method of oxidation of alcohols to their corresponding carbonyl derivatives with dimethyl sulfoxide (DMSO) and certain acid anhydrides. This method appears to be a general one and is particularly useful for the oxidation of sterically hindered hydroxyl groups. In addition this procedure has certain advantages over other oxidative methods, especially with compounds such as indole alkaloids which are sensitive to nonselective oxidizing reagents.[2]

In general the oxidation is carried out by allowing a mixture of 1 mmole of primary or secondary alcohol, 3 ml. of DMSO, and 2 ml. (*ca.* 20-mmole excess) of acetic anhydride to stand at room temperature for 18–24 hr. Thus yohimbine (1) undergoes oxidation to give yohimbinone[3,4] (2) consistently in 80–85% yields[5];

(1) A previous study of oxidation of alcohols: J. D. Albright and L. Goldman, *J. Org. Chem.*, **30**, 1107 (1965).
(2) For a discussion of oxidation of secondary alcohols in the indole alkaloid field see ref. 1.
(3) Literature compounds were identified by agreement of their physical constants with published values.
(4) M.-M. Janot, R. Goutarel, E. W. Warnhoff, and A. Le Hir, *Bull. soc. chim. France*, 637 (1961).
(5) An especially mild Oppenauer oxidation of yohimbine gave yohimbinone in 51% yield (ref. 4); yohimbine was oxidized by means of N,N'-dicyclohexylcarbodiimide, DMSO, and phosphoric acid to give yohimbinone in about 80% yield (ref. 1).