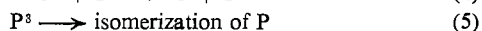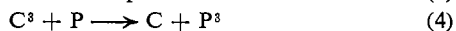significantly by the addition of oxygen and 1,3-pentadiene (piperylene). The decrease in 4-pentenal resulting from the addition of oxygen was equal to a corresponding increase in the formation of organic peroxide. No additional products were formed upon addition of piperylene but isomerization of the piperylene did occur and the piperylene concentration remained constant during photolysis.

The dependence of the 4-pentenal yield on piperylene concentration was studied. A mechanism as shown in eq. 1 through 5 could account for the 4-pentenal production. C and P are cyclopentanone and piperylene, respectively, and the superscripts 1 and 3 represent excited singlet and triplet electronic states. Applica-

$$C + h\nu \longrightarrow C^1 \qquad (1)$$
$$C^1 \longrightarrow C^3 \qquad (2)$$
$$C^3 \longrightarrow 4\text{-pentenal} \qquad (3)$$
$$C^3 + P \longrightarrow C + P^3 \qquad (4)$$
$$P^3 \longrightarrow \text{isomerization of P} \qquad (5)$$

tion of the steady-state approximation to these equations yields eq. 6 relating the quantum yield (ϕ) of 4-pentenal and the concentration of piperylene (P). k' is a

$$\frac{1}{\phi} = \frac{1}{k'} + \frac{k_4(P)}{k_3 k'} \qquad (6)$$

collection of constants, and k_4 and k_3 are the reaction rate constants for reactions 4 and 3, respectively. A plot of $1/\phi$ vs. (P) gives a straight line and the ratio k_4/k_3 is calculated to be 21 ± 8 M^{-1}.

LaPaglia and Roquitte[8] have reported measuring fluorescence from cyclopentanone both in the liquid and vapor but have reported measuring phosphorescence only in the liquid and solid. Thus spectroscopic evidence for the triplet state in liquid cyclopentanone is available. Hammond and co-workers[9] postulate that the isomerization of piperylene by cyclopentanone and other sensitizers is caused by a transfer of energy from the triplet state of the sensitizer to the ground state piperylene molecule. Our experimental results confirm their work with the cyclopentanone–piperylene system. Oxygen is known to be an effective quencher of the triplet state and low concentrations of ferric chloride have been reported[10] to be relatively ineffective as a triplet quencher. The absence of a wave length effect in our experiments would indicate the dissipation of the excess energy to a common energy state as the precursor of the 4-pentenal, most probably the lowest-lying triplet state of cyclopentanone.

In the γ-radiolysis study of cyclopentanone by Dugle and Freeman,[5] the effect of piperylene on the radiolysis yield of 4-pentenal was investigated. A set of reactions similar to eq. 1 through 5 was postulated and the rate constant ratio k_4/k_3 was reported[5] as 20 M^{-1}. The remarkable agreement between this value, taken from radiolysis data, and that found in our photolytic work points strongly to the lowest-lying triplet state as the precursor to at least part of the 4-pentenal produced in the radiolysis[11] and most, if not all, of the 4-pentenal produced in the photolysis. We believe that these

data provide the first identification of the excited-state precursor of a radiolytic product which is supported by quantitative rate constant ratios.[12] It must be remembered that this would not necessarily be an identification of the initial excited state produced in the radiolysis, only the precursor of 4-pentenal. In view of Platzman's "superexcited" states[13] which are postulated to be important precursors in radiation chemistry and to be capable of reacting before de-excitation to lower-lying electronic states, it is important to note the relatively large value of the radiolytic yield, G(4-pentenal) = 0.7. However, the 4-pentenal yield represents only a part of the total primary radiolytic yield of cyclopentanone decomposition, a major part of this being the formation of an uncharacterized oil.[4,14] Preliminary experiments with the oil found in the photolysis of cyclopentanone show a close similarity of the mass spectrum of the photolytic oil with that found for the radiolytic oil. Additional experiments are being carried out on the kinetic and chemical nature of these oils.

Further support for the triplet state precursor of 4-pentenal in the photolysis and radiolysis of cyclopentanone is provided by a comparison of the 4-pentenal yields in deoxygenated vs. air-saturated cyclopentanone solutions. The same fractional reduction in 4-pentenal yields is found in the photolysis and in the radiolysis.[4] Additional experiments are in progress on this system. Details of these and other studies on the above systems will be reported elsewhere.[7]

(12) A. Singh and G. R. Freeman, J. Phys. Chem., 69, 666 (1965), have also postulated a triplet precursor of 5-hexenal in the radiolysis of cyclohexanone on the basis of radiolytic evidence.
(13) R. L. Platzman, Radiation Res., 17, 419 (1962).
(14) D. L. Dugle and G. R. Freeman, Trans. Faraday Soc., 61, 1166 (1965).

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Reactions of Deprotonated Ligands.
I. Methylation of Deprotonated Ethylenediamine[1,2]

Sir:

We report here preliminary data on the formation of N-methylethylenediamine and N,N'-dimethylethylenediamine from deprotonated ethylenediamine ligands associated with Pt^{2+} ion.

Bipyridylethylenediamineplatinum(II) iodide, [Pt(bipy)(en)]I$_2$, was prepared by a minor modification of the method suggested by Morgan and Burstall[3] by suspending 3.10 g. of [Pt(bipy)Cl$_2$][3] in 40 ml. of 25% aqueous ethylenediamine and heating until solution was complete. The clear yellow solution was cooled to 30°, treated with a 10% excess of NaI in 20 ml. of water, cooled to 10°, and filtered. The yellow solid [Pt(bipy)(en)]I$_2$ was recrystallized from water and dried for 24 hr. in vacuo over Mg(ClO$_4$)$_2$. The yield was 3.35 g. or 70% based on [Pt(bipy)Cl$_2$]; X-ray diffraction data for this and the compounds that follow are given in Table I.

(1) This work was supported by the U. S. Atomic Energy Commission and the Robert A. Welch Foundation.
(2) en = ethylenediamine; (en-H) = a deprotonated en ligand; en-CH$_3$ = N-methylethylenediamine; en(CH$_3$)$_2$ = N,N'-dimethylethylenediamine; bipy = 2,2'-bipyridyl.
(3) G. T. Morgan and F. H. Burstall, J. Chem. Soc., 965 (1934).

(8) S. R. LaPaglia and B. C. Roquitte, Can. J. Chem., 41, 287 (1963); J. Phys. Chem., 66, 1739 (1962).
(9) G. S. Hammond, N. J. Turro, and P. A. Leermakers, ibid., 66, 1144 (1962).
(10) (a) R. B. Cundall, and P. A. Griffiths, Discussions Faraday Soc., 36, 111 (1963); (b) G. Porter and M. R. Wright, ibid., 27, 18 (1959).
(11) Dugle and Freeman[5] postulate that only 70% of the 4-pentenal arises from the triplet state.

Table I. X-Ray Diffraction Data

[Pt(bipy)(en)]I₂		[Pt(bipy)(en-H)]I		[Pt(bipy)(en-2H)]	
d, Å.	I/I_0	d, Å.	I/I_0	d, Å.	I/I_0
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	0.3[a]	3.63	0.7	2.46	0.2[a]
3.23	0.3	3.30	0.4	2.21	0.2
3.14	0.4	2.91	0.2[a]	2.02	0.2
2.53	0.5	2.49	0.2		

[Pt(bipy)(en-CH₃)]I₂·0.5H₂O		[Pt(bipy)en(CH₃)₂]I₂	
d, Å.	I/I_0	d, Å.	I/I_0
8.13	0.3[a]	5.13	0.7
6.87	0.3	4.27	1.0
5.91	0.3	4.00	0.2[a]
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).