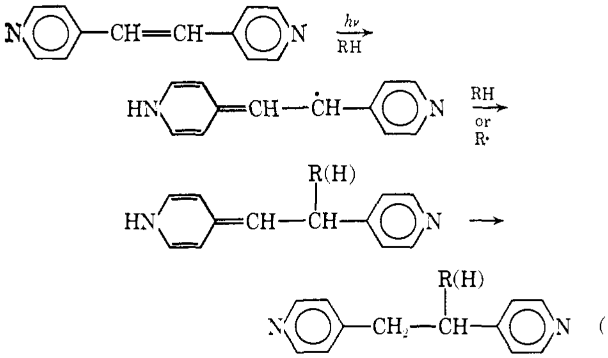
abstraction by excited **1** and subsequent reaction (addition or hydrogen abstraction) of the intermediate radical. Stilbene does not participate in analogous reactions; a mechanism involving direct hydrogen abstraction by an ethylenic carbon is rather unattractive. By analogy with photoreactions of other N-heterocyclic compounds[6,8,12] we suggest formation of **2** and **3** involves hydrogen abstraction by nitrogen and subsequent rearrangement of the initial product (eq 2).



(2)

Excited triplets of **1** are evidently not involved in formation of **2** and **3**; irradiation of 2-propanol or methylcyclohexane solutions containing sensitizers such as triphenylene or Michler's ketone and **1** leads only to *cis–trans* isomerization even on very long-term irradiation. The question of singlet participation in the reaction is less easily resolved. Absorption spectra of **1** are nearly identical in all the solvents listed in Table I. In principle, comparison of quantum efficiencies for reduction, fluorescence, and isomerization of **1** in the presence and absence of hydrogen atom donors should enable determination of the excited states responsible for each process. Although the efficiency of reduction of **1** in methylcyclohexane appears too low for it to show competition with fluorescence and intersystem crossing, the actual efficiency of initial hydrogen abstraction is probably much higher. In fact, fluorescence and isomerization efficiencies are essentially unchanged by changing solvent from benzene to methylcyclohexane. In 2-propanol and acetonitrile–water the weak fluorescence of **1** is very slightly enhanced over that in benzene. Isomerization efficiencies increase markedly when the solvent is changed from the hydrocarbons to 2-propanol or acetonitrile–water. The most significant aspect of these findings is that both isomerization and reduction are uncoupled from fluorescence; each of these processes apparently originates from some later-obtained state. A tempting possibility is that the lifetime of the fluorescent (π,π^*) singlet of **1** is shortened by rapid internal conversion to a lower n,π^* singlet. We suggest that photoreduction and photoaddition occur *via* hydrogen abstraction by this n,π^* singlet and that isomerization occurs from the triplet.[13] If n,π^* singlets are hidden due to their extremely weak oscillator strength, it is reasonable that in the absence of hydrogen atom donors they should decay nonradiatively to the ground state.

Attempts to determine whether hidden n,π^* singlets are a general phenomenon for other N-heteroaromatics are in progress. Recent studies[16] indicate that the photoreduction of acridine does not originate from either the fluorescent (π,π^*) singlet or the triplet; here again a hidden $^1n,\pi^*$ state is the probable reactant.[17]

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[12] F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, **91**, 3103 (1969).

[13] Although other explanations could be advanced, a possible explanation for the enhanced isomerization efficiency is that increases in energy of the $^1n,\pi^*$ state in polar solvents facilitate rapid $^1n,\pi^*$ $^3\pi,\pi^*$ intersystem crossing.[14] Interestingly, CNDO-II molecular orbital calculations[15] suggest that lowest excited states of **1** are n,π^*.

[14] See, for example, M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).

[15] L. G. Pederson, D. G. Whitten, and M. T. McCall, *Chem. Phys. Lett.*, **3**, 569 (1969).

[16] Y. J. Lee and D. G. Whitten, unpublished results.

[17] Support of this work by the Army Research Office (Durham) (Grant No. DA-ARO-D-31-124-G1097) and the National Institutes of Health (Grant No. GM 15,238-01,2) is gratefully acknowledged.

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Heat of Nitrogen Binding with Ruthenium(II)–Ammine Complexes

Sir:

The discovery[1] of $[Ru(NH_3)_5N_2]^{2+}$ and $[(H_3N)_5RuN_2Ru(NH_3)_5]^{4+}$ and the remarkable stability of these ions have prompted a number of recent investigations.[2-4] The enthalpy of coordination of N_2 should provide some insight into the nature of interaction of molecular nitrogen with ruthenium.

Solutions of $[Ru(NH_3)_5H_2O]^{2+}$ ranging in concentration from 0.1 to 0.03 *M* were prepared by the reduction of $[Ru(NH_3)_5Cl]^{2+}$ with zinc amalgam in 0.1 *M* H_2SO_4 under an atmosphere of argon. The $[Ru(NH_3)_5Cl]Cl_2$ was prepared from commercial anhydrous $RuCl_3$ by a slight modification of the method of Allen, *et al.*[5] One gram of $RuCl_3$ was dissolved in 12 ml of H_2O, 10 ml of $N_2H_4 \cdot H_2O$ (85%) was added, and the mixture was stirred for 1 hr. The mixture was then refluxed for 1 hr, allowed to stand overnight, and filtered by gravity; then 10 ml of 6 *N* HCl was added to the filtrate. This solution was refluxed for 1 hr and the $[Ru(NH_3)_5Cl]Cl_2$ was removed by filtration, washed, and dried.

The addition of nitrogen to $[Ru(NH_3)_5H_2O]^{2+}$ was followed in a gas reaction microcalorimeter[6] by adding N_2 to a solution of $[Ru(NH_3)_5H_2O)^{2+}$ in 0.1 *M* H_2SO_4. The formation of $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5N_2(NH_3)_5Ru]^{4+}$ was confirmed spectrally. The calorimeter used was capable of measuring heats of a few millicalories attending the uptake of a few micromoles of N_2, as followed manometrically.[6]

The heat per mole of N_2 uptake is due to a possible combination of two reactions.

$$[Ru(NH_3)_5H_2O]^{2+} + N_2 \xrightarrow{k_m} [Ru(NH_3)_5N_2]^{2+} + H_2O \tag{1}$$

$$[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{2+} \xrightarrow{k_D} [(NH_3)_5RuN_2Ru(NH_3)_5]^{4+} + H_2O \tag{2}$$

Both of these reactions have been followed kinetically[3] with rate constants determined at 20° as $k_m = 4.4$

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[1] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

[2] D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

[3] I. S. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).

[4] D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 2706 (1967).

[5] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *ibid.*, **89**, 5595 (1967).

[6] S. Boyle, M. S. Thesis, University of Colorado, 1969.

$\times 10^{-5}$ sec^{-1} [1 atm of N_2] and $k_D = 4.2 \times 10^{-2}$ l. mole^{-1} sec^{-1}. Since $k_m[N_2] \ll k_D[Ru(NH_3)_5OH_2^{2+}]$ in the experiments performed, the steady state concentration of the monomeric species is established with a half-time determined by the pseudo-first-order constant $k_D[Ru(NH_3)_5OH_2^{2+}] \cong 4.2 \times 10^{-3}$ sec^{-1} at 0.1 *M* $Ru(NH_3)_5OH_2^{2+}$ (a typical concentration); for this condition $t_{1/2} \cong 3$ min. Measurements of heat production after ~10 min correspond, therefore, to the overall reaction.

$$N_2(g) + 2Ru(NH_3)_5OH_2^{2+} \longrightarrow (H_3N)_5RuN_2Ru(NH_3)_5^{4+} + 2H_2O \quad (3)$$

Observations were made over a total of 1–2% reaction. No account was taken of reversibility of the reactions, which were studied kinetically[3] to much greater extent of reaction than employed here. Experiments were run on two concentrations of the aquo complex, 0.1 and 0.03 *M*. Different partial pressures of nitrogen were also used so that various rates of nitrogen uptake were followed. The results for the steady state heat/mol of N_2 are given in Table I. As can be seen from these results a value of −25 ± 2 kcal is obtained. The range of error must be regarded as an indication of the difficulty of measuring the small heats attending this reaction. There is no significant effect of the threefold concentration change outside of experimental error in these measurements. We therefore believe that conditions were clearly established where the heat effect is due to dimer formation and the enthalpy value of reaction 3 is −25 ± 2 kcal/mol.

Table I

Concn, *M*	$\Delta N_2/\Delta t$, μmol/sec	Heat/mol of N_2, kcal/mol
0.1	0.0020	−25 ± 2
0.1	0.0033	−26 ± 2
0.1	0.0036	−27 ± 2
0.03	0.0014	−22 ± 2
0.03	0.0011	−23 ± 2

The heat of reaction of dissolved nitrogen with the aquo ruthenium complex may be calculated from the above results. The heat of nitrogen dissolution

$$N_2(g) + aq \longrightarrow N_2(aq)$$

is estimated as −3.2 kcal at 25° from the temperature dependence of the Henry's law constants.[7] Therefore the reaction

$$N_2(aq) + 2Ru(NH_3)_5OH_2^{2+} \longrightarrow [(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$$

has a ΔH value of −22 ± 2 kcal at 25°.

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(7) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 256.

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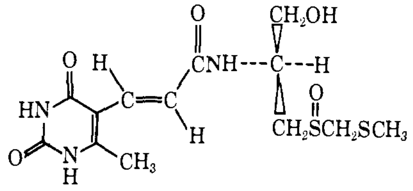
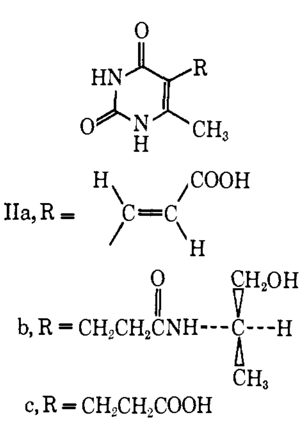
The Structure of Sparsomycin[1]

Sir:

The isolation of the antibiotic, sparsomycin, was reported some years ago by Argoudelis and Herr.[2] This communication presents evidence which establishes the structure of sparsomycin to be that represented by the expression I.



I



The previously reported molecular formula for sparsomycin was $C_{13}H_{19-21}N_3O_6S_2$. It has been found that material which gives an analysis corresponding to the suggested molecular formula contains about 0.75 mol of water per mol of sparsomycin. Antibiotic dried under high vacuum at room temperature for 48 hr or more loses 80–90% of its water and gives analytical values[3] corresponding to the molecular formula $C_{13}H_{19}N_3O_5S_2$ which must be the correct one.

Mild acid hydrolysis of sparsomycin (2 *N* acid on the steam bath) resulted in isolation of a compound (IIa) having the molecular formula $C_8H_8N_2O_4$; mp 265° dec; pK_a's (DMF–60% EtOH) 7.90 and 11.35; $\lambda_{max}^{H_2O}$ 293 mμ (ε 14,210); $\lambda_{sh}^{H_2O}$ 270 mμ (ε 12,700); ν_{max} 3420, 3010, 1750, 1700, 1645, 1590, 1345, 1315, 1200, 1095, 1030, 992, 886, 785, and 722 cm^{-1}; nmr (DMF-d$_7$) δ 2.40 (s, 3 H), 7.25 (d of d, 2 H, J = 16 Hz), 10.0–11.6 (broad exchangeable H). The mass spectrum showed no molecular ion, but the methyl ester (prepared by the Fischer procedure, mp 305–307° dec) gave 210.0676. The spectral and analytical data derived from the eight-carbon acid are consistent with structure IIa which was synthesized by the following sequence. Chromic oxide oxidation of 5-hydroxymethyl-6-methyluracil gave 5-formyl-6-methyluracil, dec above 200°; infrared carbonyl band at 1740 cm^{-1}; $\lambda_{max}^{H_2O}$ 231 mμ (ε 6440) and 283 mμ (ε 9500); nmr (DMF-d$_7$) δ 2.54 (s, 3 H), 9.98 (s, 1 H). A Wittig reaction of the aldehyde with carbethoxymeth-

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[1] This work was supported by Contracts PH43-62-168 and PH43-68-1023, with Chemotherapy, National Cancer Institute, National Institutes of Health, Bethesda, Md.

[2] A. D. Argoudelis and R. R. Herr, *Antimicrob. Ag. Chemoth.*, 780 (1962).

[3] All compounds gave either satisfactory combustion analyses or molecular formulas by mass spectrometry.