pared by gradually adding a 5×10^{-3} M Cr^{2+} solution to an equal volume of a well-stirred solution containing 5.5×10^{-3} M Fe(III) and 4.5×10^{-3} M SCN^-. Solutions prepared in this manner are green, while solutions of $CrNCS^{2+}$ are purple.[8] The absorption spectra of $CrNCS^{2+}$ and $CrSCN^{2+}$ are similar, except that the maxima in the spectrum of $CrSCN^{2+}$ are shifted about 40 mμ toward longer wave lengths. The direction of this shift is expected[9] on the basis of the weaker ligand field strength of sulfur-bonded compared to nitrogen-bonded thiocyanate and is additional evidence for the generally accepted view that the stable chromium(III) isomer is nitrogen bonded. Since the above solutions do not contain excess chromium(II) they are relatively stable. However, on standing the $CrSCN^{2+}$ undergoes aquation (64%) and isomerization (36%) with an over-all rate constant of about 7.7 $\times 10^{-5}$ sec.$^{-1}$.

If it is assumed that the exchange of chromium between Cr^{2+} and $CrNCS^{2+}$ proceeds via remote attack by chromium(II),[2] then the equilibrium constant for the isomerization is simply the ratio of the rate constants

$$CrSCN^{2+} \rightleftharpoons CrNCS^{2+} \quad K_1 \qquad (1)$$
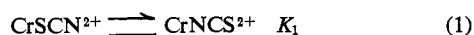
for the $Cr^{2+} + CrSCN^{2+}$ and $Cr^{2+} + CrNCS^{2+}$ reactions. Using the rate constant for the latter reaction determined by Ball and King[2] gives $K_1 = 3 \times 10^5$ at 25.0° and ionic strength 1.0 M. The nitrogen-bonded isomer is therefore about 7.5 kcal. mole^{-1} more stable than the sulfur-bonded isomer.

Some relevant rate constants are presented in Table I. It is apparent from this table that the rate constants for the formation of the isomers from chromium(III)

Table I. Rate Constants for Some Chromium(III) and Iron(III) Reactions at 25.0° and $(HClO_4) = 1.0$ M

Reaction	k, M^{-1} sec.$^{-1}$	Ref.
$FeNCS^{2+} + Cr^{2+}$	$\geqslant 2 \times 10^7$	This work
$Fe^{3+} + Cr^{2+} + SCN^-$	$\sim 2 \times 10^5$ [a]	This work
$FeN_3^{2+} + Cr^{2+}$	$\geqslant 2 \times 10^7$	This work
$CrSCN^{2+} + Cr^{2+}$	42	This work
$CrNCS^{2+} + Cr^{2+}$	1.4×10^{-4}	d
$CrN_3^{2+} + Cr^{2+}$	6.1 [b]	e
$CrNCS^{2+} + H_2O$	9.2×10^{-9} [b,c]	f
$CrSCN^{2+} + H_2O$	4.8×10^{-5} [c]	This work
$Cr^{3+} + SCN^-$	3×10^{-8}	This work
$Cr^{3+} + NCS^-$	1.8×10^{-6} [b]	f
$CrSCN^{2+} \rightarrow CrNCS^{2+}$	2.9×10^{-5} [c]	This work

[a] Units are M^{-2} sec.$^{-1}$. [b] Ionic strength $= 0.5$ M. [c] Units are sec.$^{-1}$. [d] Reference 2. [e] R. Snellgrove and E. L. King, Inorg. Chem., 3, 288 (1964). [f] C. Postmus and E. L. King, J. Phys. Chem., 59, 1208 (1955).

and thiocyanate differ by a factor of 60, while the rate constants for the dissociation of the isomers differ by a factor of about 10^4. This shows that the difference in the stabilities of the isomers is due mainly to their rates of aquation. It may also be noted that, while the CrN_3^{2+}–Cr^{2+} exchange is faster than the $CrNCS^{2+}$–Cr^{2+} reaction, the exchange is not as fast as the $CrSCN^{2+}$–

(8) J. H. Espenson has also observed a green color near the end point of titrations of chromium(II) with iron(III) solutions containing thiocyanate (personal communication).

(9) C. E. Schäffer, Special Publication No. 13, The Chemical Society, London, 1959, p. 153.

Cr^{2+} reaction. This illustrates, among other factors, the importance of allowing for any differences in the standard free energy changes when comparing the rates of inner-sphere reactions.

Finally, these studies do not establish the structure of the stable monothiocyanate complex of iron(III) because the chromium(II) may attack the complex at either the adjacent or the remote position. However, the formation of $CrSCN^{2+}$ suggests that the stable isomer of iron(III) is nitrogen bonded. If the stable isomer were sulfur bonded we would expect a 100% yield of $CrNCS^{2+}$ provided remote attack on $FeSCN^{2+}$ predominated over adjacent attack. However, this is by no means certain because adjacent attack might be more likely on the nonlinear $FeSCN^{2+}$ than on the linear $FeNCS^{2+}$.

Further studies of the properties of $CrSCN^{2+}$ and of unstable isomers produced in other oxidation–reduction reactions are in progress.

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The Role of the Triplet Excited State in the Photolysis and Radiolysis of Liquid Cyclopentanone[1]

Sir:

We have reported previously[2] an interest in the correlation of the photolysis and radiolysis of cyclopentanone. The mechanism postulated by Srinivasan[3] for the formation of 4-pentenal in the gas phase photolysis via a low vibrational level of an excited singlet state seemed to offer a unique system for study of excited states in radiation chemistry. In the Co-60 γ-radiolysis of liquid cyclopentanone, 4-pentenal has been found as a major primary product.[4,5] According to the Srinivasan mechanism[3] 4-pentenal should be the only major photolytic product in the liquid phase.

In recent investigations[6,7] we have found that, with the exception of an oil, which may be a secondary product, 4-pentenal is the major primary photolytic product in liquid cyclopentanone. These studies were carried out at both 3130 and 2537 Å. and quantum yields for 4-pentenal were 0.37 ± 0.01 and 0.38 ± 0.02, respectively. Minor primary products ($<<1$ %) were found to be 1-butene and CO with 3130-Å. radiation and 1-butene, CO, ethylene, and cyclobutane at 2537 Å.

Additional experiments showed the 4-pentenal quantum yields to be insensitive to the addition of allyl alcohol, n-hexane, ethylene, carbon monoxide, 1-butene, DPPH, and low concentrations of ferric chloride. However, the 4-pentenal quantum yield was lowered

(1) This research was supported by the U. S. Atomic Energy Commission.

(2) M. Katayama, J. C. Whitmer, and C. N. Trumbore, J. Am. Chem. Soc., 84, 4025 (1962).

(3) (a) R. Srinivasan, Advan. Photochem., 1, 83 (1963); (b) S. Cremer and R. Srinivasan, J. Am. Chem. Soc., 86, 4197 (1964).

(4) W. W. Bristowe, M. Katayama, and C. N. Trumbore, J. Phys. Chem., 69, 807 (1965).
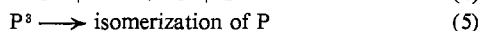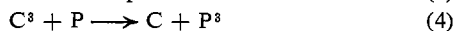
(5) D. L. Dugle and G. R. Freeman, Trans. Faraday Soc., 61, 1174 (1965).

(6) P. Dunion, Ph.D. Thesis, University of Delaware, 1965.

(7) P. Dunion and C. N. Trumbore, to be submitted for publication.

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-

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

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

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

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 $21 \pm 8 \ M^{-1}$.

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

(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.

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).