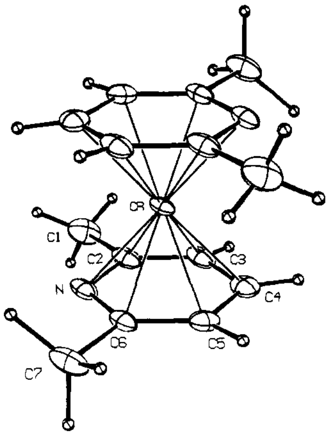

Figure 1. A view of the triclinic form (A) of $(C_7H_9N)_2Cr$. The Cr atom resides at a site of C_i symmetry. Selected bond lengths (Å): Cr-N = 2.151 (6), Cr-C(2) = 2.129 (8), Cr-C(3) = 2.128 (7), Cr-C(4) = 2.161 (8), Cr-C(5) = 2.130 (9), Cr-C(6) = 2.116 (8).

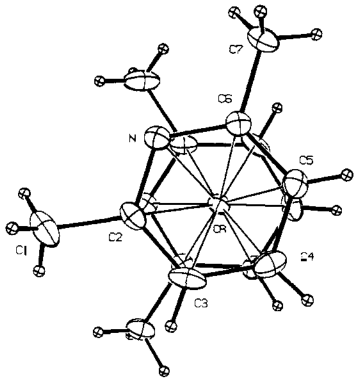

Figure 2. A view of the orthorhombic form (B) of $(C_7H_9N)_2Cr$ normal to the pyridine rings and to the C_2 axis which contains Cr. Note the staggered disposition of methyl carbons C(1) and C(7). Selected bond lengths (Å): Cr-N = 2.131 (3), Cr-C(2) = 2.126 (4), Cr-C(3) = 2.137 (3), Cr-C(4) = 2.134 (4), Cr-C(5) = 2.164 (4), Cr-C(6) = 2.125 (3).

crystal form B, the molecule resides on a twofold rotation axis that passes through the Cr atom and is parallel to the N-C(4) line. Hence, the rings are again strictly parallel, but now, as shown in Figure 2, methyl groups C(1) and C(7) are staggered.

Corresponding geometrical features of the complex in forms A and B are in good agreement.[8] For example, the mean Cr to ring atom distances are 2.136 (15) Å in A and 2.136 (10) Å in B. For sake of comparison, the mean Cr-C distances in dibenzenechromium[9] and benzenechromium tricarbonyl[10] are 2.142 (2) and 2.243 (14) Å, respectively. The least-squares planes calculated through the pyridine atoms show that these rings are planar in A, but slightly boat-shaped in B with atoms N and C(4) disposed (by 0.025 (3) and 0.033 (4) Å) toward Cr. In A methyl carbons C(1) and C(7) lie out of the pyridine planes (by 0.03 (1) Å) and away from Cr, but in B such displacements of atoms C(1) and C(7) are not apparent.

N-Methylpyrrole does not react with chromium atoms under the conditions of our experiment. However, pyridine, 2,6-difluoropyridine, and borazine react with chromium using the metal atom synthesis technique. In these cases, the products have not yielded to characterization using conventional methods; they possess low volatility and appear to be marginally stable. Further experiments are underway to prepare and characterize heterocyclic π-complexes of other transition metals, which will be reported elsewhere.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP-37028) for the purchase of the Syntex $P2_1$ diffractometer and the Robert A. Welch Foundation (Grants No. F-233 and F-081).

References and Notes

(1) K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. H. Stubbs, *J. Organomet. Chem.*, **1**, 471 (1964).
(2) (a) P. L. Pauson and A. R. Qazi, *J. Organomet. Chem.*, 7, 321 (1967); (b) E. O. Fischer and K. Öfele, *Z. Naturforsch. B*, **14**, 376 (1959).
(3) E. O. Fischer and K. Öfele, *Chem. Ber.*, **93**, 1156 (1960).
(4) R. E. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 796 (1964).
(5) P. L. Timms, *J. Chem. Soc. A*, 2526 (1970).
(6) V. Graves and J. J. Lagowski, *Inorg. Chem.*, in press, and references therein.
(7) Crystallographic experimental procedures were essentially as delineated in: P. E. Riley and R. E. Davis, *Inorg. Chem.*, **14**, 2507 (1975).
(8) Full details of the crystallographic investigations will appear elsewhere.
(9) E. Keulen and F. Jellinek, *J. Organomet. Chem.*, **5**, 490 (1966).
(10) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **29**, 2516 (1973).

L. H. Simons, P. E. Riley, R. E. Davis, J. J. Lagowski*
Department of Chemistry, The University of Texas
Austin, Texas 78712

Received November 10, 1975

On the Energy Threshold and Population Mechanism of One Metastable Methane Ion

Sir:

We wish to give detailed information about a metastable transition as observed from CH_4^+, under electron impact, in a double focusing mass spectrometer used in the defocusing mode.[1] The process which has been studied in both the normal and perdeuterated forms of the molecule is:

$$CH_4{\cdot}^+ \rightarrow CH_3^+ + H{\cdot}$$

A counting technique has been used for the energy threshold determinations. The thresholds are obtained at low source pressure (2×10^{-6} Torr) by the vanishing current method. The vanishing currents observed for ions of several of the noble gases are used as a calibration of the electron energy scale. The results are as follows. (a) The metastable ion decay has been observed to be an essentially unimolecular process. (b) The metastable peak observed for this process exhibits a thermal kinetic energy distribution (about 5 meV energy release, measured from the width at half-height). A weak component of width corresponding to an energy release of about 100 meV is only detectable at source pressures higher than 1×10^{-5} Torr. The peak widths are not in disagreement with more detailed values recently published by Solka, Beynon, and Cooks.[2] (c) The appearance potential (AP) of the fragments formed from metastable ions (16.0 ± 0.5 eV) is much higher than the AP for CH_3^+ ions formed by a fast process (14.25 ± 0.02 eV).[3] See Figure 1. (d) By using the ion source of the mass spectrometer in the Čermăk mode,[4] we have been able to detect charge transfer processes, as reported in Table I.

Intensities are expressed as the ratio of the peak height observed with the charge exchange gas present and absent. The table shows evidently that a metastable peak, corresponding to a process which is not observed under electron impact, is weakly induced by charge exchange between Kr^+ and CH_4. On the other hand charge exchange does not lead to production of metastable ions in the energy range corresponding to the AP of metastable ions observed under electron impact (i.e., with Ar^+, N_2^+, H_2^+).

These observations induce us to interpret the situation as follows. (a) Under electron impact, the metastable transition remains undetected near the threshold energy corre-

Table I

Primary ions	Recombination energies (eV)	Dissociative charge exchange[a] Fast process CH_3^+ intensity	Metastable process CH_3^+ intensity
Xe^+	$^2P_{3/2}$, 12.13; $^2P_{1/2}$, 13.436	–	–
Kr^+	$^2P_{3/2}$, 13.999; $^2P_{1/2}$, 14.69	+ (20)	+ (1.6)
Ar^+	$^2P_{3/2}$, 15.759; $^2P_{1/2}$, 15.937	+ (9)	–
N_2^+	$X^2\Sigma_g^+$, 15.576; $A^2\Pi_u$, 16.693	+ (10.5)	–
H_2^+ [5]	16.4–17.4; 13–14	+ (5.5)	–
Ne^+	21.564	+ (2)	–
He^+	24.586	+ (1.7)	–

[a] Key: (+) CE takes place; (−) CE does not take place.

sponding to formation of CH_3^+ ions by a fast process (14.25 eV). (b) A weak metastable transition is induced by quasi-resonant charge-exchange with Kr^+. The metastable ions responsible for this peak pertain to the lowest possible energy threshold for the appearance of the CH_3^+ formed by a fast process (14.25 ± 0.02 eV). (c) Under electron impact, the main metastable transition is only observed as the electron energy approaches 16 eV. Owing to the impossibility of inducing its appearance by charge-exchange and owing to the lack of excited states of $CH_4{\cdot}^+$ at energies below 22 eV, it is postulated that to populate the metastable state requires a superexcited state of CH_4.

This conclusion is strongly favored by some experimental facts. (1) For He resonance line photons, the cross section for ionization of CH_4 is negligibly small between 16 and 17 eV;[6] a process giving excited CH_4^+ directly cannot, thus, be expected in this energy range. (2) For resonance photons a small but definitely present absorption band between 16 and 17 eV has been detected.[7] (3) The first derivative of the $CH_4{\cdot}^+$ ionization curve, as taken with quasi-monoenergetic electrons by Morrison,[8] shows autoionized structures starting in the range of 15.5 eV; this confirms unpublished results obtained in our laboratory.[9]

From this discussion, the metastable transition cannot any longer be considered as pertaining to the threshold mechanism for the appearance of CH_3^+ ions, but it is more probably due to a cascade process, such as:

$$CH_4 + e^- \rightarrow CH_4^*$$

$$CH_4^* \rightarrow CH_4{\cdot}^+ + e^- \rightarrow CH_3^+ + H{\cdot}$$

The CH_3^+ ions should be vibrationally excited. A vibrational excitation of about 1.75 eV is not unacceptably high, as the fragmentation process $CH_3^+ \rightarrow CH_2{\cdot}^+ + H{\cdot}$ requires at least 5.38 eV in excess of the threshold energy necessary to produce CH_3^+. These results require some more comments. They show that the occurrence of the metastable ions in methane is not bound with the minimum value of the rate constant for the lowest energy process, as given by the R.R.K.M. theory: $k_{\min} = 1/hN(E_0)$. The R.R.K.M. theory might well not apply to the decay of the $CH_4{\cdot}^+$ ions, owing to the high symmetry of these ions and the relatively small number of oscillators able to randomize the excitation energy.[10,11] Calculations give such a high $k_{\min}$ value (7.8×10^8 s^{-1}) that no metastable ion could be observed. Some attempts have been made to lower this $k_{\min}$ value by considering either potential energy barrier surmounting[12] or tunneling.[13] However, Solka et al.[2] have recently refuted these processes as well as the possibility of a low rate electronic predissociation mechanism. They have measured the temperature effect on the kinetic energy release and have shown that the best interpretation is the occurrence of a centrifugal barrier for the decomposition of the CH_4^+ ion. We do not think this opinion to be in contradiction with our observations. We suggest that in a first step, a radiationless transition occurs from a superexcited state of CH_4 to a region of the $CH_4{\cdot}^+$ ion potential hypersurface outside the Franck–Condon region. Vibrationally excited $CH_4{\cdot}^+$ ions obtained in this way should be able to decay into vibrationally excited CH_3^+ ions and H atoms. The low rate observed for the dissociation should be due, as suggested by Solka et al., to the occurrence of a centrifugal barrier. A radiationless transition from a super-excited state of CH_4 has been postulated some years ago as an origin for the abnormal vibrational population of $CH_4{\cdot}^+$.[14]

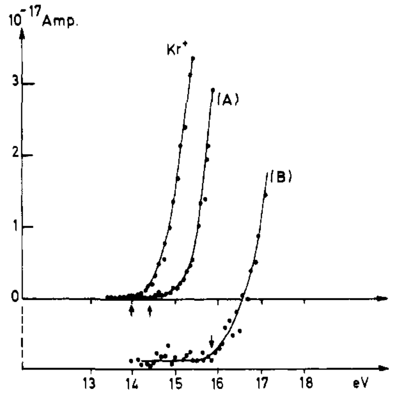

Figure 1. AP of the CH_3^+ ions: (A) fast process; (B) metastable process, sensitivity ×100. Pressure of CH_4, 2×10^{-6} Torr; Kr, 0.6×10^{-6} Torr.

On the other hand, metastable ions corresponding to the lowest possible energy for the process $CH_4{\cdot}^+ \rightarrow CH_3^+ + H{\cdot}$, are formed by charge transfer processes (with Kr^+ ions) and do not appear from electron impact. This may mean that the selection rules for charge transfer (at least to polyatomic molecules) and for electron impact ionization are quite different. It would not be surprising that this charge transfer should take place through some transient complex formation, the lifetime of which being at least of the order of a rotational period (10^{-12} s). Such a complex can be deduced from recent experiments on the dynamics of charge transfer reactions between Kr^+ and CH_4 as described by Herman.[15] From the complete scattering diagram, a small but real isotropic scattering (some percent of the prominent thermal $CH_4{\cdot}^+$ peak) is detected in any angle about the center of mass. This isotropic contribution could reflect the formation of metastable $CH_4{\cdot}^+$ ions with internal energy ranging in the vicinity of the lowest energy process for the appearance of CH_3^+ as observed in our experiments.

Our results show up the importance of carefully measuring the appearance potentials of metastable ions, relative to the lowest threshold for the corresponding ions formed by fast processes. On occasion, calculations involving a higher energy threshold for the appearance of the metastable ions have to be made.

Acknowledgments. We are indebted to the F.N.R.S. and to the F.R.F.C. for their financial support to one of us (J. P. Flamme) and to our laboratory. We sincerely thank the referees for suggesting improvements and discussions about the first version of this letter.

References and Notes

(1) See ref 3 in *Int. J. Mass Spectrom. Ion Phys.*, **7**, 227 (1971).
(2) B. H. Solka, J. H. Beynon, and R. G. Cooks, *J. Phys. Chem.*, **79**, 859 (1975).
(3) V. H. Dibeler, M. Krauss, R. Reese, and F. N. Harllee, *J. Chem. Phys.*, **42**, 3791 (1965).

(4) V. Cernak and Z. Herman; *Nucleonics*, **19**, 106 (1961).
(5) E. Gustafson and E. Lindholm, *Ark. Fys.*, **18**, 219 (1960).
(6) C. R. Brundle, M. B. Robin, and H. Basch; *J. Chem. Phys.*, **54**, 2196 (1970); B. P. Pullen, T. A. Carlson, W. E. Moddeman, et al., *J. Chem. Phys.*, **53**, 768 (1970).
(7) E. E. Koch and M. Skibowski, *Chem. Phys. Lett.*, **9**, 429 (1971).
(8) J. D. Morrison and J. C. Traeger, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 289 (1973).
(9) E. Derouane, Memoire de Licence, Université de Liège, 1965, J. P. Flamme and R. Locht, unpublished results.
(10) M. Krauss, A. L. Wahrhaftig, and H. Eyring, *Rev. Nucl.*, **5**, 241 (1955).
(11) H. M. Rosenstock, *Adv. Mass Spectrom.*, **4**, 523 (1968).
(12) L. P. Hills, M. L. Vestal, and J. H. Futtrell, *J. Chem. Phys.*, **54**, 3834 (1971).
(13) C. E. Klots, *J. Phys. Chem.*, **75**, 1526 (1971); (b) *Chem. Phys. Lett.*, **10**, 422 (1971).
(14) W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, 5H, 4256 (1971).
(15) Z. Herman, V. Pacak, and K. Birkinshaw, American Society of Mass Spectroscopy Meeting, 23d Annual Conference, Paper K.9 (1975).

J. P. Flamme, J. Momigny,* H. Wankenne
Laboratoire d'Etude des Etats Ionisés
Département de Chimie Générale, University of Liège
Liège, Belgium

Received July 23, 1975

Electron and Energy Transfer Mechanisms in the Quenching of the Tris(2,2'-bipyridine)ruthenium(II) Luminescence by Cyanide Complexes

Sir:

Efficient quenching of electronically excited coordination compounds can take place by either energy or electron transfer.[1,2] In the case of the emitting state of tris(2,2'-bipyridine)ruthenium(II), $^*\mathrm{Ru(bpy)_3}^{2+}$, the following potentially efficient quenching processes may thus be expected:

$$^*\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Q} \xrightarrow{k_{\mathrm{en.t.}}} \mathrm{Ru(bpy)_3}^{2+} + {}^*\mathrm{Q} \quad (1)$$

$$^*\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Q} \xrightarrow{k_{\mathrm{red}}} \mathrm{Ru(bpy)_3}^{+} + \mathrm{Q}^{+} \quad (2)$$

$$^*\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Q} \xrightarrow{k_{\mathrm{ox}}} \mathrm{Ru(bpy)_3}^{3+} + \mathrm{Q}^{-} \quad (3)$$

The "thermodynamic" barriers for these reactions may be evaluated knowing that the energy difference between $^*\mathrm{Ru(bpy)_3}^{2+}$ and $\mathrm{Ru(bpy)_3}^{2+}$ is 17.1 kK (2.12 eV),[3] and that the reduction potentials of the $^*\mathrm{Ru(bpy)_3}^{2+}$-$\mathrm{Ru(bpy)_3}^{+}$ and $\mathrm{Ru(bpy)_3}^{3+}$-$^*\mathrm{Ru(bpy)_3}^{2+}$ couples are +0.84 V[4] and −0.83 V,[4-7] respectively, vs. the NHE. Kinetic ("intrinsic") barriers are also known to be important in both energy[1,8] and electron[6,9,10] transfer reactions. Quenching of $^*\mathrm{Ru(bpy)_3}^{2+}$ by energy transfer (reaction 1) has been demonstrated for several acceptors.[1] Oxidative quenching (reaction 3) has been shown to occur with various oxidants,[6,11-13] whereas only indirect evidence has so far been obtained for the reductive quenching (reaction 2), using $\mathrm{S_2O_4}^{2-}$, $\mathrm{Ru(NH_3)_6}^{2+}$, and $\mathrm{Fe(CN)_6}^{4-}$ as quenchers.[4] We describe here the results obtained from the quenching of $^*\mathrm{Ru(bpy)_3}^{2+}$ by several cyanide complexes which were chosen because they span a wide range of excited-state energies and redox potentials (Table I), and we report definite evidence for the occurrence of reaction 2.

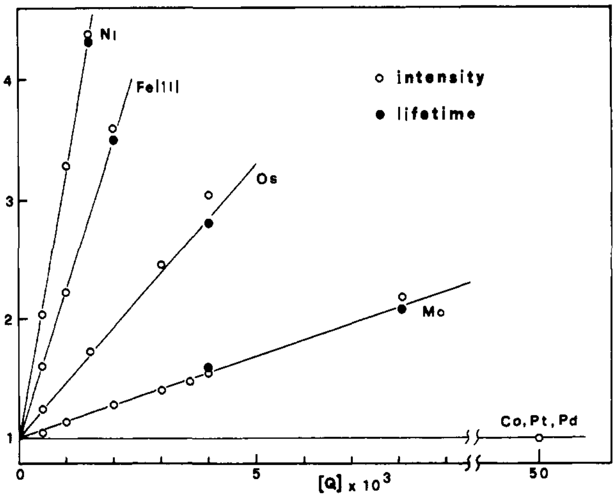

Figure 1. Stern–Volmer plots for the quenching of the $^*\mathrm{Ru(bpy)_3}^{2+}$ luminescence by cyanide complexes (see Table I).

Quenching of the $^*\mathrm{Ru(bpy)_3}^{2+}$ luminescence (intensity and lifetime) and the photochemical experiments were carried out in aerated aqueous solutions at pH 4, μ = 0.50 (NaCl), and 23°. The Stern-Volmer quenching plots are shown in Figure 1. The quenching rate constants, calculated using τ^0 = 400 ns, are collected in Table I together with some values obtained by other authors.

Solutions containing the highest concentration of $\mathrm{Mo(CN)_8}^{4-}$, $\mathrm{Os(CN)_6}^{4-}$, and $\mathrm{Ni(CN)_4}^{2-}$ used in the quenching experiments were irradiated in a conventional photochemical apparatus with 464-nm light. For the $\mathrm{Ru(bpy)_3}^{2+}$-$\mathrm{Mo(CN)_8}^{4-}$ system, irradiation caused an increase in pH while the absorption spectrum decreased at λ <255 nm and increased at about 270 and 390 nm, indicat-

Table I. Quenching of $^*\mathrm{Ru(bpy)_3}^{2+}$ by Various Cyanide Complexes[a]

Quencher Q	$E(^*\mathrm{Q})$,[b] kK	$E^0(\mathrm{Q^+/Q})$,[c] V	$E^0(\mathrm{Q/Q^-})$,[c] V	k_q,[d] $\mathrm{M^{-1}\,s^{-1}}$	Reaction[e]
$\mathrm{Mo(CN)_8}^{4-}$	19.6[f]	+0.73[g]	(<−1.8)[h]	3.4×10^8	2
$\mathrm{Cr(CN)_6}^{3-}$	12.4[i]	—	−1.28[j]	7.5×10^8 [k]	1
$\mathrm{Fe(CN)_6}^{4-}$	23.7[l]	+0.36[j]	(< −1.7)[t]	3.3×10^9 [m]	2
$\mathrm{Fe(CN)_6}^{3-}$	23.5[l]	(> + 0.75)[n]	+0.36[j]	6.5×10^9 [o]	3
$\mathrm{Co(CN)_6}^{3-}$	26.0[p]	—	−0.83[j]	<10^6	—
$\mathrm{Os(CN)_6}^{4-}$	47[l]	+0.75[j]	—	1.2×10^9	2
$\mathrm{Ni(CN)_4}^{2-}$	23[q]	(> +1.0)[n]	−1.35[r]	5.6×10^9	1 or 2
$\mathrm{Pd(CN)_4}^{2-}$	22.7[i,s]	(> +1.0)[n]	(< − 1.8)[h]	<10^6	—
$\mathrm{Pt(CN)_4}^{2-}$	23.0[i,s]	—	—	<10^6	—

[a] $E(^*\mathrm{Ru(bpy)_3}^{2+})$ = 17.1 kK, E^0 ($^*\mathrm{Ru(bpy)_3}^{2+}$-$\mathrm{Ru(bpy)_3}^{+}$) = +0.84 V, E^0 ($\mathrm{Ru(bpy)_3}^{3+}$-$^*\mathrm{Ru(bpy)_3}^{2+}$) = −0.83 V. [b] Lowest energy absorption feature, unless otherwise noted. [c] Reduction potential at 25° and μ = 0, unless otherwise noted. [d] 23°, μ = 0.50. [e] Reaction responsible for the quenching (see text). [f] From ref 14. [g] "Stability Constants of Metal-Ion Complexes", *Chem. Soc., Spec. Publ.*, **No. 17** (1964). [h] Electroinactive up to the indicated potential at the mercury electrode in deaerated 0.50 M NaCl solution, 25°. [i] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970). [j] D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964, p 237. [k] F. Bolletta, M. Maestri, and L. Moggi, *J. Phys. Chem.*, **77**, 861 (1973). [l] From ref 18. [m] This value is in agreement with that reported in ref 4. [n] Electroinactive up to the indicated potential at the platinum electrode in deaerated 0.50 M NaCl solution, 25°. [o] 25°, ref 4. [p] H. Kataoka, *Bull. Chem. Soc. Jpn.*, **46**, 2078 (1973); K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, **13**, 1543 (1974). [q] From ref 14 and 25. [r] Half-wave potential vs. the SCE, from A. A. Vlček, *Collect. Czech. Chem. Commun.*, **22**, 948 (1957). [s] Energy of the lowest excited state from emission spectra. [t] A. N. Frumkin, *Trans. Faraday Soc.*, **55**, 156 (1959).