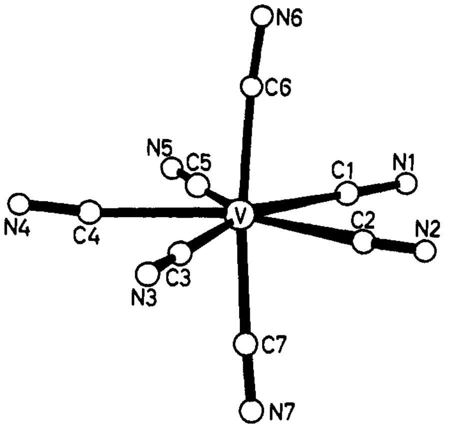

Figure 1. The structure of the $[V(CN)_7]^{4-}$ anion.

chosen as $I1$ with lattice constants $a = 9.229\ (1)$ Å, $b = 9.097\ (1)$ Å, $c = 9.341\ (1)$ Å, $\alpha = 90.02\ (1)°$, $\beta = 92.49\ (1)°$, and $\gamma = 90.00\ (1)°$. The calculated density assuming $K_4[V(CN)_7]\cdot 2H_2O$ is 1.80 g/cc, which compares favorably with the observed density of 1.77 ± 0.02 g/cc. Diffractometer data were collected with Mo Kα radiation to a maximum 2θ of 45°. The structure was solved by Patterson methods, and the atomic coordinates and anisotropic thermal parameters were refined by block-diagonal least-squares techniques to a final R value of 0.025. Table I lists the individual distances and angles found.

Table I. Principal Bond Distances and Angles for the $[V(CN)_7]^{4-}$ Anion

	Distances,[a] Å		
V–C(1)	2.134 (8)	C(1)–N(1)	1.155 (12)
V–C(2)	2.155 (7)	C(2)–N(2)	1.139 (10)
V–C(3)	2.152 (7)	C(3)–N(3)	1.143 (10)
V–C(4)	2.152 (7)	C(4)–N(4)	1.146 (10)
V–C(5)	2.150 (7)	C(5)–N(5)	1.137 (10)
V–C(6)	2.131 (8)	C(6)–N(6)	1.148 (11)
V–C(7)	2.156 (8)	C(7)–N(7)	1.147 (11)
	Angles,[b] °		
C(1)–V–C(2)	72.5 (3)	V–C(2)–N(2)	179.0 (7)
C(1)–V–C(5)	72.5 (3)	V–C(3)–N(3)	178.5 (7)
C(2)–V–C(3)	72.3 (3)	V–C(4)–N(4)	177.9 (7)
C(3)–V–C(4)	70.5 (3)	V–C(5)–N(5)	179.3 (6)
C(4)–V–C(5)	72.3 (3)	V–C(6)–N(6)	172.2 (2)
C(6)–V–C(7)	171.0 (3)	V–C(7)–N(7)	172.8 (7)
V–C(1)–N(1)	179.5 (9)		

[a] Estimated standard deviations × 10^3 in parentheses. [b] Estimated standard deviations × 10 in parentheses.

The structure of the anion is a pentagonal bipyramid of approximate D_{5h} symmetry as illustrated in Figure 1. The average ∠C–V–C for adjacent carbons in the equatorial plane is 72.0 ± 0.6°. The two axial cyanides are not colinear but instead give rise to $\angle C_{ax}\text{–}V\text{–}C_{ax} = 171.0°$. The average $V\text{–}C_{eq}$ distance is 2.149 ± 0.006 Å and the average $V\text{–}C_{ax}$ distance is 2.144 ± 0.012 Å, thus indicating no significant difference in the length of the equatorial and axial bonds. There are two distinct V–V distances of 7.87 and 8.10 Å. The potassium ions are arranged in an approximate tetrahedral arrangement about the vanadium; two of the distances are 4.44 Å and the other two are 4.15 Å All other interatomic distances are normal The standard deviation of the distances of the vanadium and the five equatorial carbons from a least-squares plane of these atoms is 0.031 Å with C(4) the greatest distance from the plane at 0.047 Å

It should also be noted that the V–C distances of 2.15 Å are the longest we know of for a first-row transition metal cyanide complex. However, the Cr(III)–C distance in the seven-coordinate $[Cr(O_2)_2(CN)_3]^{3-}$ anion is 2.09 Å,[16] and a V(III)–C bond is expected to be longer. This is the first definitive example of a seven-coordinate complex of a first-row transition metal containing seven identical ligands and the first ML_7 type complex in which L is a ligand other than fluoride. It is interesting to speculate that the compound $K_4Mo(CN)_7\cdot 2H_2O$, for which coordination number seven has been suggested,[17] may have the same structure as $K_4[V(CN)_7]\cdot 2H_2O$.

The structure of the anion persists in solution as evidenced by the fact that the electronic spectra are very similar in solution and in the solid state.[11,13] The difficulty encountered by Perumareddi, *et al.*,[18] in assigning the d–d electronic transitions based on O_h symmetry for the V(III) cyanide complex is therefore explained. More recently, Alexander and Gray[19] discussed the electronic structure, but they too assumed octahedral geometry. A reinterpretation of the electronic spectrum of $V(CN)_7^{4-}$ and a discussion of its electronic properties in light of this new structural evidence will be forthcoming.

Acknowledgments. We wish to acknowledge support of this research by the Research Corporation.

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A Gas-Phase Photon-Induced Ion–Molecule Reaction Studied by Ion Cyclotron Resonance Spectroscopy

Sir:

The intermolecular reactions of photoexcited molecules have been studied photochemically for many decades for their mechanistic as well as synthetic interest.[1] More recently photoelectron spectroscopy[2] has shown that many cations have excited states accessible using visible and ultraviolet light. We wish to report the observation of a gas-phase photon-induced ion–molecule reaction and to interpret the wavelength dependence of the photochemical product as a probe of the absorption spectrum of the $C_3H_5^+$ cation.

The reaction observed was

$$C_3H_5^+ + C_2H_4 \xrightarrow{h\nu} C_3H_7^+ + C_2H_2 \qquad (1)$$

An ion cyclotron resonance spectrometer was used to produce cations from ethylene neutrals and to observe the light-induced cation products. The spec-

(1) See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

(2) D. W. Turner, *et al.*, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

trometer has been described previously[3,4] as having modifications for studying light-induced processes.[4,5] A 2.5 kW xenon arc with wavelength selection by interference filters constituted the photon source.

The ion-molecule reactions of ethylene have been extensively studied by ion cyclotron resonance and other techniques.[6] The following reactions are known to occur

$$C_2H_4^+ + C_2H_4 \rightarrow (C_4H_8^+)^* \begin{cases} \rightarrow C_4H_7^+ + H & (2a) \\ \rightarrow C_3H_5^+ + CH_3 & (2b) \end{cases}$$

and

$$C_3H_5^+ + C_2H_4 \rightarrow (C_5H_9^+)^* \begin{cases} \xrightarrow{M} C_5H_9^+ & (3a) \\ \rightarrow C_5H_7^+ + H_2 & (3b) \end{cases}$$

In both reactions an excited complex is formed which can either decompose or, at least in the case of $(C_5H_9^+)^*$, be collisionally stabilized.[6] Under the conditions of this experiment the peak height of the $C_3H_5^+$ cation (without light) was about four times that of $C_2H_4^+$.

Photon-induced processes were observed by recording ion cyclotron resonance spectra with and without light, and typical results are shown in Figure 1. Alternatively, it was possible to monitor the intensity of one mass peak as a function of irradiating wavelength.

Ion cyclotron double resonance,[7] which has proven valuable in elucidating ion–molecule reactions, was used to identify the reactant ion in reaction 1. In the double resonance experiment the reactant ion is irradiated in the analyzer, leading to larger cyclotron orbits for the reactant ion. If the orbit is large enough, the ion will hit the cell plates and be ejected. Such an ejection technique has been successful in identifying reactants in photon-induced processes.[4] With 4000-Å photons illuminating the cell, and the detector monitoring $C_3H_7^+$, the only double resonance signal observed with an irradiating field of 0.06 V/cm (peak-to-peak) identified $C_3H_5^+$ as the reactant ion. Ejection of $C_3H_5^+$ made the $C_3H_7^+$ signal almost completely disappear.[8]

Using a recent value[9] for the ΔH_f of $C_3H_5^+$, reaction 1 is 3 or 22 kcal/mol endothermic, depending upon whether the isopropyl or *n*-propyl cation is formed.[10] Increasing the electron energy in 10-eV increments to 70 eV has no effect on the very small $C_3H_7^+$ peak. An increase in electron energy presumably increases the internal excitation of the $C_2H_4^+$ reactant in reaction 2, but apparently the excess energy in the $(C_4H_8^+)^*$ complex that is partitioned to the $C_3H_5^+$ product is insufficient to make reaction 1 proceed.[11]

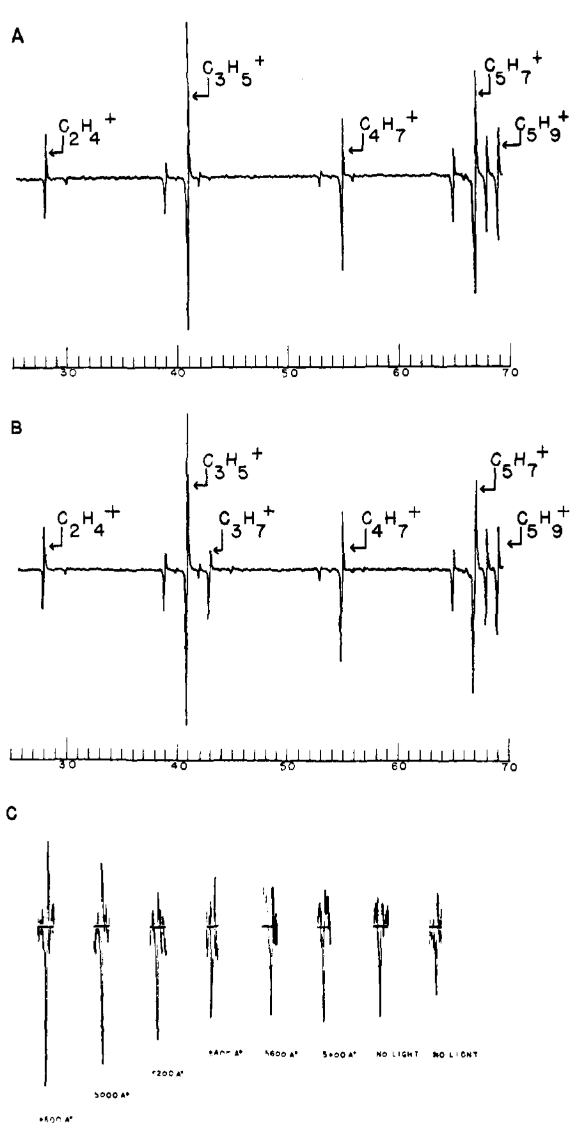

Figure 1. (A) A field swept ion cyclotron resonance (icr) spectrum of C_2H_4 from *m/e* 26 to *m/e* 69. Experimental parameters: C_2H_4 pressure, 6.3 × 10^{-8} Torr; electron energy, 12.2 eV; trapping voltage, 1.7 V. (B) Same as (A) except for illumination of the icr cell with 4000-Å photons. The increase of $C_3H_7^+$ (*m/e* 43) is due to a photon-induced process. (C) Field swept spectra of the $C_3H_7^+$ peak showing the photoproduction threshold region. The lower field half of the derivative peak shape provided the best measure of peak intensity. Interference filters (100-Å bandpass, 200 Å apart) provided wavelength selected light.

The photochemical onset for production of $C_3H_7^+$ is 5200 Å (55 kcal/mol) as shown in Figure 1C. The photoproduction of $C_3H_7^+$ increases smoothly with

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(7) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(8) The double resonance result does not rule out photodissociation of $(C_5H_9^+)^*$, but that possibility seems highly unlikely. The dissociation lifetime of $(C_5H_9^+)^*$ is $\sim 10^{-4}$ sec (ref 6a) and *only* when ions are trapped for seconds is the photon-induced reaction observed. If photodissociation of the intermediate $(C_5H_9^+)^*$ were to occur, normal icr residence times of milliseconds would be sufficient for observation of the photodissociation product. In addition, ejection of the unexcited $C_5H_9^+$ cation produced no change in the $C_3H_7^+$ signal and, hence, photodissociation of the unexcited $C_5H_9^+$ cation to $C_3H_7^+$ is ruled out.

(9) G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Amer. Chem. Soc.*, **92**, 254 (1970).

(10) All other ΔH_f's from J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, Washington, D. C., June 1969.

(11) Professor J. L. Beauchamp has proposed an alternative interpretation of our data. He suggested that the $C_2H_4^+$ cation might absorb a photon and react with C_2H_4 in reaction 2b to form excited $(C_3H_5^+)^*$, which would then react with C_2H_4 in reaction 1 to form the $C_3H_7^+$ product observed. To test this hypothesis a transient ejection experiment was necessary because complete ejection of $C_2H_4^+$ would also eliminate $C_3H_5^+$ formed in reaction 2b. With the detector monitoring $C_3H_7^+$, the electron beam was turned off, $C_2H_4^+$ ejected, and the light turned on. Approximately the same transient $C_3H_7^+$ signal was observed with and without $C_2H_4^+$ ejection. However, when the experiment was repeated and $C_3H_5^+$ ejected instead of $C_2H_4^+$, no $C_3H_7^+$ product signal was observed showing that it is the $C_3H_5^+$ cation which is absorbing a photon and not the $C_2H_4^+$ cation.

increasing photon energy and at 4000 Å (72 kcal/mol) shows no signs of leveling off. The curve shows no structure at 200-Å resolution.

Presumably the photon-induced reaction goes through the $(C_5H_9^+)^*$ complex. Any observation of product means that the $C_3H_5^+$ cation *must have* absorbed a photon, since C_2H_4 is transparent to below 3500 Å.[12] The $C_3H_7^+$ onset at 55 kcal/mol is higher than the endothermicity of reaction 1 by at least 33 kcal/mol. Hence, the threshold for the photon-induced reaction is not determined by the endothermicity of the reaction. The $C_3H_7^+$ onset may be determined either by the absorption of a photon by $C_3H_5^+$ or by the competitive unimolecular decomposition of $(C_5H_9^+)^*$. In either case, electronic excitation of the $C_3H_5^+$ by light must be possible at wavelengths at least as long as 5200 Å.

Reaction 2b is calculated[10] to be 6.5 kcal/mol endothermic for the formation of the cyclopropyl cation and 3.5 kcal/mol exothermic for the formation of the allyl cation.[9] Although internally excited $C_2H_4^+$ in reaction 2b may be energetically capable of producing the endothermic cyclopropyl cation product, it is quite possible that even if the cyclopropyl cation is formed, it rearranges to the more stable allyl structure[13] (especially on the time scale of our reactions (seconds)). More significantly, three different investigations[6,14] have presented experimental evidence which indicates that $C_3H_5^+$ produced in reaction 2b is formed in an exothermic reaction. It seems likely that allyl cation is the only possible exothermic product of this reaction, and hence we infer from these investigations[6,14] that the $C_3H_5^+$ ion whose electronic excitation we have studied is the allyl cation. (We cannot, however, completely rule out participation of the cyclopropyl or other isomeric cations.) Accordingly, we consider our results to provide evidence for the existence of an excited state of the allyl cation lying about 2.5 eV above the cation ground state.

Experimental data on the electronic spectrum of the allyl cation are very limited. Attempts have been made to observe the electronic spectrum of the allyl cation in highly acidic solutions.[15] The allyl cation system contains impurities and the ultraviolet spectrum is not known.[15] However, 1,1,3,3-tetramethylallyl cation is reported to show an absorption with maximum at 3050 Å (4.1 eV) in H_2SO_4.[15]

Semiempirical π-electron calculations for the allyl cation typically show the lowest excited singlet state lying near 5 eV.[16] Two recent theoretical calculations,[16,17] which explicitly consider σ excitations, indicate that excited states involving σ electrons lie as low or even lower in energy than the excited states that arise from excitation of a π electron. Our evidence for a low-lying excitation supports the need for explicit consideration of σ electrons in theoretical calculations for the allyl cation.

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A New and Unique Chemical Source of Singlet Molecular Oxygen. Potassium Perchromate

Sir:

Potassium perchromate was first prepared and isolated in 1905 by Riesenfeld, *et al.*,[1] who found that this unusual salt liberates oxygen in aqueous solution according to the following equation.

$$4CrO_8^{3-} + 2H_2O \longrightarrow 4CrO_4^{2-} + 7O_2 + 4OH^-$$

The crystal structure of K_3CrO_8, determined by Stomberg and Brosset in 1960,[2] showed that the perchromate ion has D_{2d} ($\bar{4}2m$) symmetry and consists of a chromium ion in oxidation state (5+) surrounded by four peroxide groups (O_2^{2-}) in which the geometrical arrangement of the oxygen atoms around chromium is dodecahedral.[3]

Foote[4] has speculated that an enzyme bound or metal bound form of singlet oxygen might be the reactive species in certain biological oxygenations. We now wish to report unequivocal spectral evidence that potassium perchromate, upon aqueous decomposition, releases oxygen in the excited singlet state. In addition, chemical evidence is presented which demonstrates that at least some of the O evolved, either by simultaneous formation and decomposition of the salt or from the aqueous decomposition of the pure, dry salt, results in typical singlet oxygen reactions. We believe that the results, presented here for potassium perchromate, represent the first demonstration of a transition metal–oxygen complex which releases oxygen in the excited singlet state.

When a basic solution of potassium chromate is added to an aqueous methanol solution of H_2O_2 and 2,3-dimethylbutene-2 at 5°,[5] a red-brown solid begins to form, indicating formation of K_3CrO_8, with a simultaneous slow effervescence which increases upon warming the solution to room temperature. From the solution, 2,3-dimethyl-3-hydroperoxybutene-1 can be isolated in 35% yield whose infrared and nmr spectra are identical with those of the product from sensitized photooxidation.

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[5] Potassium chromate (16.9 g, 0.087 mol) and potassium hydroxide (3.5 g, 0.065 mol) in 200 ml of water were slowly added at 5° to 300 ml of 33% aqueous methanol containing 30 ml of 30% hydrogen peroxide and 2.1 g (0.025 mol) of 2,3-dimethylbutene-2.