

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FLORIDA STATE UNIVERSITY]

The Infrared Spectrum and Structure of Hexacyanodinickelate(I) Ion,¹ $[\text{Ni}_2(\text{CN})_6]^{-4}$ BY MOSTAFA F. AMR EL-SAYED² AND RAYMOND K. SHELINÉ

RECEIVED AUGUST 18, 1955

The infrared spectrum of $[\text{Ni}_2(\text{CN})_6]^{-4}$ ion has been obtained from 2.5–15 μ . The presence of absorption in the $\text{C}\equiv\text{N}$ region only, indicates that there are no $\text{C}=\text{N}$ groups in the complex anion. Four different structures are discussed. The structure with bridged $\text{C}\equiv\text{N}$ groups, using three center molecular orbitals, is found to satisfy all the experimental results, but is less energetically favorable than the Mellor and Craig structure. However, the Mellor and Craig structure does not agree with the preliminary X-ray analysis.

Introduction

In 1919, Bellucci³⁻⁶ and Corelli^{3,4} observed that when $\text{K}_2[\text{Ni}(\text{CN})_4]$ is reduced by sodium or potassium amalgam, a red color develops and a red crystalline compound may be isolated having the empirical formula $\text{K}_2[\text{Ni}(\text{CN})_3]$. Since then, the structure of this complex and the valency of nickel in it has been the subject of a great amount of discussion. Several structures have been proposed, some of which are based on the assumption that the ion is monomeric,⁷ dimeric⁸⁻¹⁰ or tetrameric.¹¹ Magnetic moment measurements⁹ indicated that the complex is diamagnetic and a dimeric structure of two square planes attached through a point was suggested. Recently, an X-ray study¹⁰ has shown even more conclusively that the anion is dimeric. This study suggested a planar structure involving bridged $\text{C}=\text{N}$ groups. If this structure is correct, two different carbon-nitrogen stretching frequencies should be observed; one representing the $-\text{C}\equiv\text{N}$ stretching frequency, the other representing the $\text{>C}=\text{N}$ stretching mode. Since the infrared spectrum has been so helpful in differentiating between $-\text{C}=\text{O}$ and $\text{>C}=\text{O}$ frequencies in the metal carbonyls,^{12,13} it seems reasonable to apply it to the analogous problem in the cyanide complexes.

Experimental

(a) **Preparation of the Sample.**—The complex $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ was prepared by two different methods¹⁴ based on the reduction of $\text{K}_2[\text{Ni}(\text{CN})_4]$. In the first method, sodium amalgam was used as the reducing agent and the crystalline substance was obtained by the slow introduction of the reduced red solution into 100 ml. of 95% ethanol. The complex was freed of $\text{K}_2[\text{Ni}(\text{CN})_4]$ and KCN by washing several times with ethanol followed by liquid ammonia.

(1) This investigation was supported by a research grant from the Office of Ordnance Research, U. S. Army, under contract No. DA-01-009-DRD-406.

(2) From portions of a thesis to be submitted by M.F.A.E. to the Graduate School of the Florida State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) I. Bellucci and R. M. Corelli, *Atti. Accad. Lincei*, **22**, [II] 485 (1913).

(4) I. Bellucci and R. M. Corelli, *Z. anorg. allgem. Chem.*, **86**, 88 (1914).

(5) I. Bellucci, *Gazz. chim. ital.*, **49**, [II] 70 (1919).

(6) I. Bellucci, *ibid.*, **49**, 285 (1919).

(7) C. L. Deasy, *THIS JOURNAL*, **67**, 152 (1945).

(8) P. Ray and H. Sahu, *J. Indian Chem. Soc.*, **23**, 161 (1946).

(9) D. P. Mellor and D. P. Craig, *Proc. Roy. Soc., N. S. Wales*, **76**, 281 (1942).

(10) R. Nast and W. Pfab, *Naturwissenschaften*, **39**, 300 (1952).

(11) R. S. Nyholm, *Chem. Revs.*, **53**, 295 (1953).

(12) R. K. Shelin and K. S. Pitzer, *THIS JOURNAL*, **72**, 1107 (1950).

(13) J. W. Cable, R. S. Nyholm and R. K. Shelin, *ibid.*, **76**, 3373 (1954).

(14) John W. Easten and M. Wayland, *ibid.*, **64**, 1187 (1942).

In the second method, metallic potassium was used as the reducing agent in liquid ammonia at its b.p. and in which an excess of $\text{K}_2[\text{Ni}(\text{CN})_4]$ had been dissolved. The bulky red precipitate was washed, by decantation, with liquid NH_3 . In both cases, the ammonia was eliminated by gentle suction after evaporation at room temperature, followed by the passage of oxygen-free nitrogen through the system.

(b) **Infrared Spectrum.**—Two major difficulties are encountered in obtaining the spectrum of this complex. The first one is the insolubility in organic solvents. The second one is the instability and its great tendency to oxidize to $\text{K}_2[\text{Ni}(\text{CN})_4]$. However, these difficulties were overcome by use of the mull technique since the rate of oxidation is greatly reduced in nujol. The absorption spectrum was taken on a Perkin-Elmer model 21 spectrophotometer using NaCl optics. The spectrophotometer was calibrated by obtaining the spectrum of water vapor in the air and checking the peaks recorded against standard values. These corrections have been applied to the reported values where necessary. The absorption curves are shown in Fig. 1.

Analysis of the Spectrum.—The infrared absorption frequencies together with the known Raman shifts¹⁵ for $[\text{Ni}(\text{CN})_3^-]_2$ and $[\text{Ni}(\text{CN})_4^-]$ are shown in Table I.

TABLE I
THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF
 $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ AND $\text{K}_2[\text{Ni}(\text{CN})_4]$

The complex	I.R. frequencies, (cm.^{-1}) mull in nujol	Raman shift, ¹⁵ (cm.^{-1}) soln.
$\text{K}_4[\text{Ni}_2(\text{CN})_6]$	2128	2142
	2079	
	2055	
$\text{K}_2[\text{Ni}(\text{CN})_4]$	2135	2144
	1625	
	1603	

Ammonia and $\text{K}_2[\text{Ni}(\text{CN})_4]$ both absorb in the 1600 cm.^{-1} region. In the spectrum obtained (Fig. 1a), a weak absorption is found in this region. In order to eliminate the possibility of this absorption being due to an NH_3 impurity, the complex was prepared by the first method without washing with liquid NH_3 , and the spectrum obtained. Even though this preparation involves no use whatever of ammonia, the same band was observed and there was no difference in its structure. After complete oxidation, the intensity of this band was increased and a spectrum similar to that of $\text{K}_2[\text{Ni}(\text{CN})_4]$ was obtained (Fig. 1b and c). This absorption might be due to the water of crystallization¹⁶ of $\text{K}_2[\text{Ni}(\text{CN})_4]$.

The maximum of the band at 2128 cm.^{-1} of $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ could not be accurately measured because of the overlap with the oxidation product absorption band at 2135 cm.^{-1} .

(15) R. Samuel and Mohd. Jan Khan, *Z. physik*, **84**, 87 (1933).

(16) Foil A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1292 (1952).

Discussion

Four possible structures are shown in Fig. 2(I-IV). The vibrational analysis of these structures as obtained from symmetry properties and group theory has been tabulated in Tables II-IV.

TABLE II
TWO COPLANAR SQUARE PLANES ATTACHED THROUGH A POINT (D_{2h})

Type	Activity	Skeletal vibrations	Designation	Non-skeletal vibrations	Designation
A_g	R	4	$\nu_1-\nu_4$	3	$\nu_5-\nu_7$
A_u	Ia	1	ν_8	1	ν_9
B_{1g}	R	2	$\nu_{10}-\nu_{11}$	2	$\nu_{12}-\nu_{13}$
B_{1u}	IR	3	$\nu_{14}-\nu_{16}$	3	$\nu_{17}-\nu_{19}$
B_{2g}	R	3	$\nu_{20}-\nu_{22}$	3	$\nu_{23}-\nu_{25}$
B_{2u}	IR	2	$\nu_{26}-\nu_{27}$	2	$\nu_{28}-\nu_{29}$
B_{3g}	R	0	...	1	ν_{30}
B_{3u}	IR	3	$\nu_{31}-\nu_{33}$	3	$\nu_{34}-\nu_{36}$

TABLE III
TWO SQUARE PLANES PERPENDICULAR TO EACH OTHER AND ATTACHED THROUGH A POINT (D_{2d})

Type	Activity	Skeletal vibrations	Designation	Non-skeletal vibrations	Designation
A_1	R	4	$\nu_1-\nu_4$	3	$\nu_5-\nu_7$
A_2	Ia	0	...	1	ν_8
B_1	R	1	ν_9	1	ν_{10}
B_2	R, IR	3	$\nu_{11}-\nu_{13}$	3	$\nu_{14}-\nu_{16}$
E	R, IR	5	$\nu_{17}-\nu_{21}$	5	$\nu_{22}-\nu_{26}$

TABLE IV
TWO SQUARE PLANES ATTACHED THROUGH AN EDGE (D_{2h})

Type	Activity	Skeletal vibrations	Designation	Non-skeletal vibrations	Designation
A_g	R	4	$\nu_1-\nu_4$	3	$\nu_5-\nu_7$
A_u	Ia	1	ν_8	1	ν_9
B_{1g}	R	1	ν_{10}	1	ν_{11}
B_{1u}	IR	3	$\nu_{12}-\nu_{14}$	3	$\nu_{15}-\nu_{17}$
B_{2g}	R	3	$\nu_{18}-\nu_{20}$	3	$\nu_{21}-\nu_{23}$
B_{2u}	IR	2	$\nu_{24}-\nu_{25}$	2	$\nu_{26}-\nu_{27}$
B_{3g}	R	1	ν_{28}	2	$\nu_{29}-\nu_{30}$
B_{3u}	IR	3	$\nu_{31}-\nu_{33}$	3	$\nu_{34}-\nu_{36}$

The number of the stretching and bending modes of the eight infrared active carbon-nitrogen vibrations which belong to each structure, as obtained by a method described in a previous work,¹³ is given below. In structure I or II there are three $C\equiv N$ stretching modes and five bending fundamentals. In structure III there are two $C\equiv N$ and one $C=N$ stretching vibrations, and three $C\equiv N$ and two $C=N$ bending modes. In structure IV the eight vibrations consist of three $C\equiv N$ stretching and five $C=N$ bending fundamentals.

An acceptable structure should satisfy the following criteria: (1) dimeric structure, (2) diamagnetism, (3) planar structure, (4) bridged configuration, (5) presence of only $C\equiv N$ groups, (6) energetically favored. Conditions 3 and 4 are based on the assumption that the preliminary X-ray analysis is correct. First we are going to discuss the four structures in terms of the first five criteria and finally we are going to compare them from the energy point of view (the last condition).

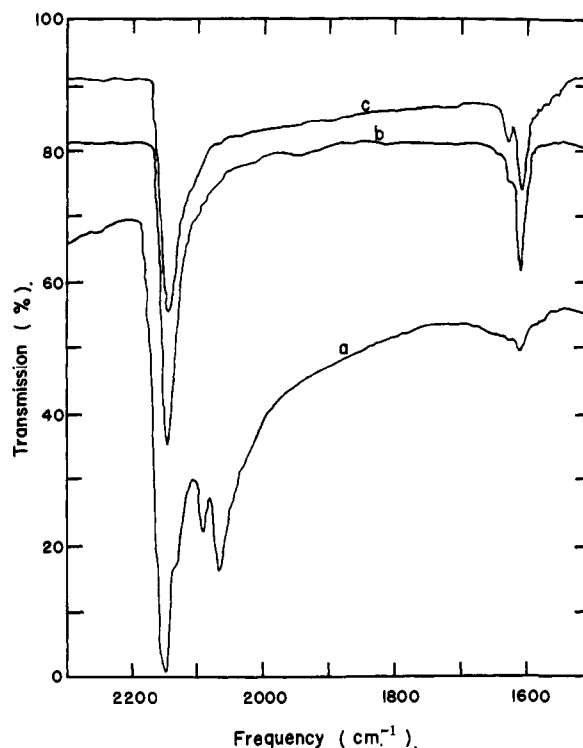


Fig. 1.—The infrared spectra of $K_4[Ni_2(CN)_6]$ and $K_2[Ni(CN)_4]$ (those portions omitted showed negligible absorption in the rock salt region): a, the infrared spectrum of $K_4[Ni_2(CN)_6]$; b, the infrared spectrum of $K_4[Ni_2(CN)_6]$ after complete oxidation; c, the infrared spectrum of $K_2[Ni(CN)_4]$.

Structure I.—The structure shown in Fig. 2(I) is proposed by Mellor and Craig⁹ on the basis that the complex is diamagnetic and there are no theoretical grounds for assuming the presence and the quenching of the unpaired electron spin by some inter- or intra-atomic interaction.

This structure is most easily visualized by assuming that each Ni(I) ion forms four dsp^2 bonds. Three of these are Ni-C coordinate covalent bonds, while the fourth is a Ni-Ni covalent bond formed from the interaction of the two half-filled hybrid orbitals on each nickel ion. Here the Ni atom is effectively bivalent, since the Ni-Ni bond is present in the anion. This structure does not satisfy condition (4). However, if there is any doubt about the X-ray analysis this structure would be strongly favored by the fact that it is formed directly from the ground state of $Ni(I)(^2D_{3/2})$. Not only does this structure require 3 infrared $C\equiv N$ stretching modes but also it suggests that these frequencies should lie lower than the corresponding frequency in the $[Ni(CN)_4]^{-2}$ ion. That is to be expected because the 4 pairs of d electrons in the $[Ni_2(CN)_6]^{-4}$ ion have only three positions available for π bonding whereas in the $[Ni(CN)_4]^{-2}$ ion they have four positions. Accordingly the Ni-C bond order and frequency in $[Ni(CN)_4]^{-2}$ ion will be correspondingly lower than in $[Ni_2(CN)_6]^{-4}$ ion, whereas the C-N bond order and frequency will be correspondingly higher. This structure also gives the most satisfactory explanation of the second criterion, diamagnetism.

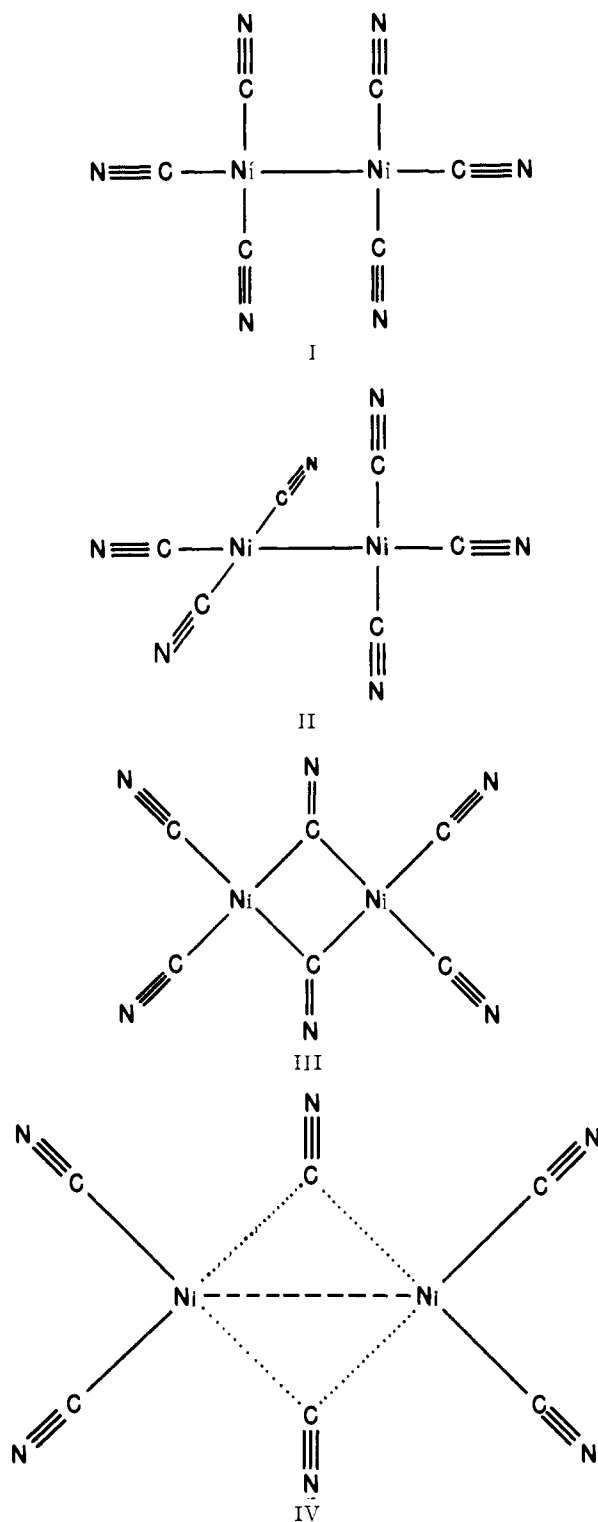


Fig. 2.—Possible structure of $K_4[Ni_2(CN)_6]$.

Structure II.—This structure is expected to be found with structure I and all the possible free rotational structures if free rotation about the Ni-Ni single bond is allowed at room temperatures. This structure would have lower energy than structure I because of the repulsion effects and that at low temperature we expect it to predominate. Unfortunately,

it does not satisfy the third and the fourth conditions.

Structure III.—The structure shown in Fig. 2(III) is proposed by Nast and Pfab¹⁰ as a result of a preliminary X-ray analysis. In this structure both nickel atoms are square coordinated and are considered to be bivalent. The nitrogen in the bridge has a covalency of two which is unusual. It is claimed that the electron deficiency is compensated for by resonance between $=\ddot{N}$ and $=\ddot{N}$: in the bridged cyanides. This structure does not satisfy condition (5) and supports, less satisfactorily, an explanation for the second condition than does either structure I or II. Moreover, it is to be noticed that more energy is required for the rehybridization of the carbon atoms of the cyanide groups which form the bridge in this structure.

Structure IV.—A fourth structure is shown in Fig. 2(IV) in which the dotted lines represent half bonds, which form the $C\equiv N$ bridge, and the broken line represents the spin coupling of the two odd electrons on the two Ni(I) ions. The bonding in this structure could be visualized in two different ways. In the first one, an electron is promoted to one of the p-orbitals and then the Ni(I) ion forms dsp^2 hybridized-orbitals. Two of these orbitals form the terminal cyanides which are considered as normal localized single bonds. According to Eberhardt¹⁷ and Duffy¹⁸ three atoms may supply three orbitals, one on each atom, and these will interact to form one bonding and two anti-bonding orbitals. Two electrons may just fill the bonding orbital constituting a three center bond. The three atoms involved in this case are two nickels and one carbon. The supplied orbitals are two vacant dsp^2 hybrid orbitals and one filled sp hybrid orbital. These form a three center bond in which the two electrons are localized between the three centers. Two of these bonds form the bridge. To account for the observed diamagnetism, the two odd promoted p-electrons on the two nickel ions must have their spins coupled. Pictorially the L.C.A.O. is represented in Fig. 3a, from which the resulting M.O. easily can be visualized.

In the second way of visualizing structure IV, the Ni(I) uses dsp hybrid orbitals in forming the skeletal frame work. Two of these orbitals form the terminal cyanides, while the third half-filled orbital forms, with the corresponding orbital of the other Ni ion, a covalent Ni-Ni bond. There are left then vacant p-orbitals in the plane of the skeletal framework which can combine with the filled sp-orbitals of the entering cyanide groups to form the bridge. Pictorially the L.C.A.O. is represented in Fig. 3b. Figure IIIb explains condition (2) better than Fig. IIIa, but the amount of overlap is very small. An amount of energy, corresponding to the promotion energy in Fig. IIIa, is required for the distortion of the p-orbitals to obtain the right direction for maximum overlap. However, Fig. IIIa gives a better explanation for the tendency of the complex to oxidize to the mononuclear $[Ni(CN)_4]^{-2}$ ion than does any other structure. Three

(17) W. H. Eberhardt, B. Crawford and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(18) G. H. Duffy, *ibid.*, **19**, 963 (1951); footnote, p. 964.

reasons seem to explain clearly this property: (a) the weak nature of the half bonds; (b) the fact that there is no change involved in the hybridization of either the nickel or the carbon in the oxidation process; and (c) the energy required to remove the promoted p-electrons is less than that which would be necessary if they were in an inner shell. Another advantage of Fig. IIIa is that there are no p-orbitals left empty, whereas in Fig. IIIb and in the other structures in Fig. II, a p-orbital is left unused after bonding. It should be pointed out that structure IV satisfies the familiar covalencies of carbon and nitrogen and that an octet of electrons surrounds each nickel atom. As usual,¹⁹ the transfer of the negative charge is accomplished by the formation of double bonds from the nickel atom to the attached terminal cyanides. The contribution of this double bond resonating form to the actual state of the $[\text{Ni}_2(\text{CN})_6]^{-4}$ should be greater than the contribution of the corresponding form to the actual state of $[\text{Ni}(\text{CN})_4]^{-2}$ ion. That is simply because the contribution of this form places a zero valent charge on the metallic atom in $[\text{Ni}_2(\text{CN})_6]^{-4}$ whereas it places a +2 charge on the central atom in $[\text{Ni}(\text{CN})_4]^{-2}$. This predicts that the terminal cyanides in $[\text{Ni}_2(\text{CN})_6]^{-4}$ would have a bond order less than the cyanides in $[\text{Ni}(\text{CN})_4]^{-2}$. The spectrum obtained agrees with this prediction if we assign the absorptions at 2079 and 2055 cm^{-1} to the terminal cyanides which have lower value if compared to 2135 cm^{-1} for the absorption of $[\text{Ni}(\text{CN})_4]^{-2}$. This means that the third absorption of $[\text{Ni}_2(\text{CN})_6]^{-4}$ ion at 2128 cm^{-1} is due to the bridged cyanides. This absorption should be at a higher frequency than that of $[\text{Ni}(\text{CN})_4]^{-2}$, since we do not assume double bond formation in the bridge. This unexpected result can be explained if we consider the nature of hybridization of the bonds in the bridge if compared to that in $[\text{Ni}(\text{CN})_4]^{-2}$. The carbon atoms of the bridged cyanides seem to form sp hybrid orbitals with some sp² character and this decreases the force constant of the bonds as well as the C-N bond order. This will shift the absorption to lower frequency.

Energy Considerations.—A simple comparison of the energies required for the formation of these structures would show that the Mellor and Craig formula is the most favorable one. In this comparison, the energy required for the formation of a certain structure is considered to be the difference between the energy used by the gaseous atoms in forming the proper orbitals for interaction and the energy which is released from such interaction in the formation of the bonds. In comparing structure I or II with structure IV, it is assumed that the energies of the C≡N bonds, the terminal Ni-C bonds and the Ni-Ni bond in structure IV are equal to the corresponding energies in structure I or II. By neglecting the height of the barrier between structure I and II, structure IV is found to require an amount of energy Q more than does either structure I or II. Q is given by the equation

$$Q = E - (4b - 2B) \quad (1)$$

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 254.

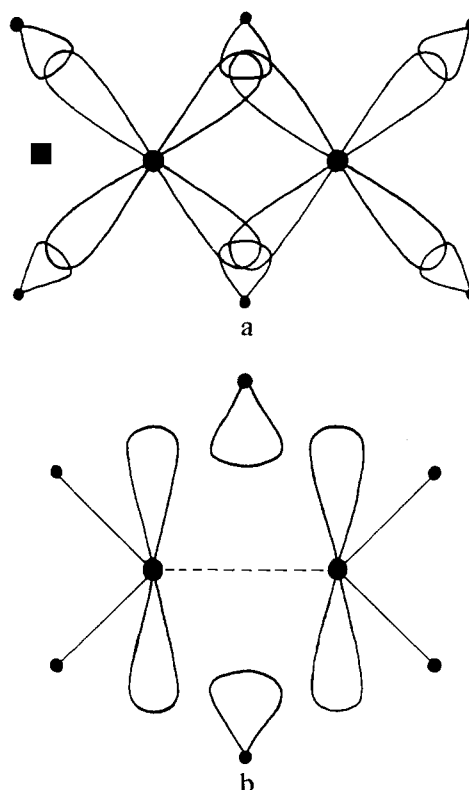


Fig. 3.—Pictorial representations for the formation of the C≡N bridge using the L.C.A.O. method. The large circles represent nickel atoms and the small ones represent the carbon atoms.

where

$$\begin{aligned} E &= \text{the promotion energy/mole, } ({}^2D \rightarrow {}^2F) \\ b &= \text{the Ni-C half-bond energy} \\ B &= \text{the Ni-C bond energy} \end{aligned}$$

It is to be expected that B is $> b$. However, for the purpose of continuing this quantitative discussion it is assumed that a maximum limit for b is B . Then equation 1 becomes

$$Q' = E - 2B \quad (2)$$

where Q' is the minimum limit of the energy difference between structure I or II and structure IV.

E is found to be²⁰ 386.78 kcal./mole and B is given the value²¹ 95 kcal./mole. From these values, the value of Q' is found to be 196.78 kcal./mole. This means that the energy required in the formation of structure IV is more than that required in forming structure I or II by an amount greater than 196.78 kcal./mole. A similar quantitative calculation with structure III is difficult to carry out because of the lack of the necessary data. However qualitatively the energy required for the gaseous atoms to form the bridge in structure III seems to be more than enough to be compensated for by the difference in bond energies.

From the above discussion, it is shown that structure IV agrees with all the experimental results, but is less energetically favorable, while structures I and II do not agree with X-ray conclusions, but

(20) C. E. Moore, "Atomic Energy Levels," Vol. II, U. S. Government Printing Office, Washington, D. C., 1952.

(21) Joe W. Cable and Raymond K. Sheline, *Chem. Revs.*, in press.

they are the most favorable structures from an energetic point of view. Consequently, the need of a complete X-ray analysis—giving bond distances and Fourier maps—is quite obvious.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

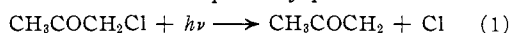
The Photolysis of Chloroketones¹

BY R. P. TAYLOR AND F. E. BLACET

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An exploratory study has been made of the photolysis of 3-chloro-2-butanone and 4-chloro-2-butanone. The α -chloro compound, although thermally more unstable, gave results analogous to those obtained for chloroacetone² with chlorine atoms being formed in the principal primary process. The β -chloro compound appears to have more carbon-carbon bond dissociation in the primary process analogous to methyl ethyl ketone. Both compounds are thermally unstable, and their photolyses were accompanied by formation of polymeric substance.

Strachan and Blacet² have investigated the photolysis of chloroacetone at 3130 Å. and found good evidence that the main primary process is



In order to compare differences in the primary process between compounds with a chlorine atom α and β to the carbonyl group, a brief study has been made of the photolyses of 3-chloro-2-butanone and 4-chloro-2-butanone.

Experimental

The α -chloro compound, 3-chloro-2-butanone, was prepared by the chlorination of 2-butanone.³ The products were a 3:1 mixture of 3-chloro-2-butanone and 1-chloro-2-butanone which were separated by fractional distillation. The β -compound, 4-chloro-2-butanone, was made by addition of acetyl chloride to ethylene.⁴ The compound was distilled several times through a column of 30 theoretical plates and at 54 mm. pressure of nitrogen. The boiling point of the distillate over the center fraction was steady at 61.8°, but after storing for a week at 0° under vacuum, analysis showed only 95% of the theoretical chlorine content. A sample left in contact with air at room temperature turned dark brown overnight and gave a strong odor of hydrogen chloride.

The photochemical apparatus and procedure was similar to that described previously.² All products were identified and analyzed with a mass spectrometer.

Results

The α -Chloro Compound, 3-Chloro-2-butanone.

—All successful photolyses were performed at 150 and 3130 Å. The major product was hydrogen chloride, its quantum yield being approximately 0.5. Small amounts of 2-butanone and carbon monoxide were also detected, quantum yields being about 0.04 and 0.02, respectively. No methane or ethane was formed. The mass spectrogram gave small peaks at M/e of 140 and 142, possibly due to $\text{CH}_3\text{COC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{COCH}_3$ and $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{COCH}_3$. A further product was a polymeric material deposited on the cell walls. Considerable quantities were deposited in attempts at runs below 150°. The polymer absorbed strongly at 3130 Å., but it was transparent at 4050 Å. and through the visible. A dark run at 150° showed hydrogen chloride was formed but in an amount

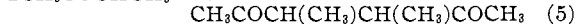
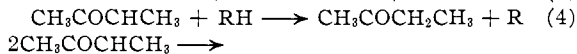
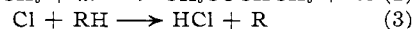
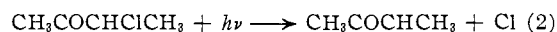
only about 5% of that obtained in photolyses under similar conditions.

The β -Chloro Compound, 4-Chloro-2-butanone.

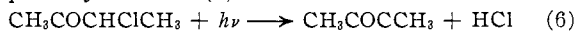
—Dark runs at 70 and 150° yielded considerable quantities of hydrogen chloride and a product giving a large peak at M/e of 70, presumably methyl vinyl ketone formed by elimination of HCl from the parent compound. A few photolyses were tried at 150° in spite of the concurrent thermal decomposition. It could not be determined whether or not hydrogen chloride was a product as so much was present from the dark reaction. However, products obtained, which were not formed in the thermal process, were methane and carbon monoxide, both with quantum yields of about 0.3. Products were also found giving peaks at M/e of 62, 64 and 66 in the correct ratios expected for chloro compounds of mass 62 and 64 with isotopic contribution at 64 and 66. Considerable polymeric material was deposited on the walls apparently from polymerization of methyl vinyl ketone but no other products could be detected.

Discussion

The photolysis mechanism for the α -chloro compound seems to be similar to that for chloroacetone²



The formation of HCl and 2-butanone is evidence for (2), (3) and (4). Reaction (5) would explain the detection of a small 142 peak. A second primary process (6), similar to that apparently observed for chloroacetone,² could account for the 140 peak by reaction (7).



The very small yield of carbon monoxide and the lack of methane indicates that the breaking of carbon-carbon bonds is of small importance as a primary process for the α -chloro compound.

The results from the β -chloro compound are complicated by the presence of a large amount of dark reaction. It seems that moving the chlorine atom further from the carbonyl group considerably reduces the tendency to be lost; otherwise secondary

(1) This work was supported by the Office of Ordnance Research.

(2) A. N. Strachan and F. E. Blacet, *THIS JOURNAL*, **77**, 5254 (1955).

(3) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 675 (1908).

(4) N. A. McGinnis and R. Robinson, *ibid.*, 405 (1941).