The Ultraviolet Absorption Spectra and Hydrolysis of Bis(acetylacetonato)nickel(II) in Dichloromethane

Kiyoshi Isobe, Yukio Nakamura, and Shinichi Kawaguchi

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka

(Received June 2, 1972)

The ultraviolet spectrum of $Ni(acac)_2$ in dichloromethane shows two maxima, at 265 and at 300 nm. The intensity ratio of these two bands is very sensitive to the water content of the solvent, the high-energy band decreasing and the low-energy band increasing with the water content. It is thus suggested that the trimeric $Ni(acac)_2$ might have only one absorption band, at 265 nm, in dichloromethane completely free from donor impurities. The UV spectrum of $Ni(acac)_2$ in dichloromethane changes with time due to the hydrolytic reaction. Even in the solvent containing 4.54×10^{-3}M water, acetylacetone was freed from the complex in the yield of 34.4% after 48 hours' standing. A minute amount of the residual complex was isolated; its tetrameric structure is suggested on the basis of its UV spectrum in methanol.

The ultraviolet spectra of thirty-one metal acetylacetonates were measured by Holm and Cotton[1] in chloroform and/or absolute ethanol in the 240—400 nm region, and were grouped into three classes. Bis(acetylacetonato)nickel(II) is present in ethanol entirely as the solvated species $Ni(acac)_2\cdot2EtOH$, and shows an absorption maximum at 294 nm ($\varepsilon=23700M^{-1}cm^{-1}$), accompanied by a shoulder on the longer-wavelength side. Similar absorption spectra were also observed for all other metal complexes except Cu(II), Fe(III), Co(III), Cr(III), and alkali metal acetylacetonates,[1] and are thought to be due to a π-π^* type transition.[2]

In chloroform, however, $Ni(acac)_2$ exhibits a very different spectrum than that in ethanol, having two maxima at 265 nm ($\varepsilon=15200$) and at 296 nm ($\varepsilon=12400$).[1] It is well established that $Ni(acac)_2$ exists as an octahedral trimer in crystals[3] and also in non-coordinating solvents.[4] The anomalous spectrum found in chloroform was explained by Cotton and Fackler[5] as due to the presence of both nonbridging and bridging chelate rings in the trimer. The former were presumed to give rise to the low-energy band at nearly the same wavelength as that of the absorption band observed in alcohol. On the other hand, the latter bridging rings were thought to cause the high-energy band, which disappears in donor solvents because of the depolymerization of the trimer.

In the course of our investigation of the reaction of $Ni(acac)_2$ with dry hydrogen bromide in dichloromethane,[6] the ultraviolet spectra of $Ni(acac)_2$ and other related compounds have been carefully examined. In this paper we will report the results we have obtained, which are different from those of Cotton and his co-workers.[1,5]

Experimental

Preparation of Complexes. *Anhydrous bis(acetyacetonato)-nikel(II), Ni(acac)$_2$*: Bis(acetylacetonato)diaquonickel(II) was prepared according to the Charles method,[7] recrystallized three times from methanol, and dehydrated by heating at 100°C *in vacuo* for 4 hr (Found: Ni, 22.82; C, 46.23; H, 5.54%).

Bis(acetylacetonato)dimethanolnickel(II), Ni(acac)$_2$(CH$_3$OH)$_2$: $Ni(acac)_2$ (2 g) was dissolved in 100 ml of light petroleum, and the mixture was refluxed for 30 min. To this solution we then added 30 ml of dry methanol and refluxed it for 30 min. The solution was then evaporated to about 40 ml and kept in a desiccator at room temperature. Sky-blue crystals were thus obtained. Found: Ni, 18.21; C, 44.43; H, 6.95%. Calcd for $C_{12}H_{22}O_6Ni$: Ni, 18.29; C, 44.90; H, 6.91%.

Bis(acetylacetonato)bis(pyridine)nickel(II), Ni(acac)$_2$py$_2$: Following the method of Hashagen and Fackler,[8] the direct reaction of $Ni(acac)_2$ with pyridine was conducted to obtain $Ni(acac)_2py_2$. Found: Ni, 14.46; C, 57.59; H, 5.87; N, 7.02%. Calcd for $C_{20}H_{24}N_2O_4Ni$: Ni, 14.14; C, 57.81; H, 5.78; N, 6.74%.

Tetrameric Complex [Ni(acac)(OCH$_3$)(CH$_3$OH)]$_4$: This compound was prepared according to the directions of Bertrand and Caine.[9] Found: Ni, 26.54; C, 37.53; H, 6.58%. Calcd for $C_7H_{14}O_4Ni$: Ni, 26.59; C, 38.58; H, 6.48%.

Presumably Tetrameric Complex Ni(acac)(OH)(H$_2$O)$_2$: $Ni(acac)_2(H_2O)_2$ (3 g, 1.02×10^{-2} mol) was dissolved in 300 ml of water, and to the mixture we added an aqueous solution (300 ml) of KOH (0.56 g, 1.00×10^{-2} mol); the resulting precipitate was separated and dried. Found: Ni, 28.35; C, 27.53; H, 5.61%. Calcd for $C_5H_{12}O_5Ni$: Ni, 27.84; C, 28.48; H, 5.74%.

Purification of Solvents. Dichloromethane and methanol were purified and dried by the standard methods.[10] The water contents of the dried solvents were determined by the Karl Fischer method to be 4.54×10^{-3} and 2.6×10^{-3}M respectively. Appropriate amounts of water was added to prepare solvents of various water contents up to 0.12M and 0.3M respectively.

Measurements. The ultraviolet absorption spectra were measured at room temperature on a Hitachi recording spectrophotometer, EPS-3T, using 1-cm quartz cells in the 210—

1) R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).
2) D. W. Thompson, *Structure and Bonding*, **9**, 27 (1971).
3) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).
4) D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961).
5) F. A. Cotton and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **83**, 2818 (1961).
6) K. Isobe, Y. Nakamura, and S. Kawaguchi, *Inorg. Nucl. Chem. Letters*, **7**, 927 (1971).
7) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).
8) J. T. Hashagen and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **87**, 2821 (1965).
9) J. A. Bertrand and D. Caine, *ibid.*, **86**, 2298 (1964).
10) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed., Volume 2 of "Techniques of Chemistry" ed. by A. Weissberger, Wiley-Interscience, New York (1970).

340 nm region. Freshly-distilled solvents were used to prepare $\sim 10^{-5}$ M solutions. The molar absorption coefficients of polymeric complexes are expressed on the basis of the gram-atom of nickel(II).

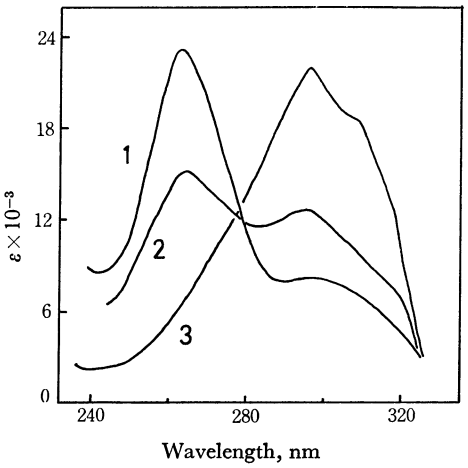

Fig. 1. Ultraviolet spectra of bis(acetylacetonato)nickel(II) in dichloromethane (curve 1), in chloroform (curve 2, ref. 5) and in methanol (curve 3).

Results and Discussion

Ultraviolet Spectra of $Ni(acac)_2$. Curve 1 in Fig. 1 represents the absorption spectrum of $Ni(acac)_2$, which was measured before 10 min after dissolution in dichloromethane containing 4.54×10^{-3}M water. The spectrum is very different from Curve 2 determined by Cotton and Fackler[5] in chloroform. The high-energy band at 265 nm is much larger (ε=23650), and the low-energy band at 300 nm is much smaller (ε=8450). This discrepancy is due not to the nature of the solvent employed, but to the difference in the water content. The peak-height ratio of the 265 and 300 nm bands decreases as the water content of dichloromethane is increased. The spectra of $Ni(acac)_2$ in dichloromethane containing 8.0×10^{-3}M water or 1.2×10^{-2}M methanol are quite similar to Curve 2 in Fig. 1. On the other hand, the peak-height ratio of the two absorption bands became even larger when dichloromethane was dried over calcium hydride for 2 days, and a $Ni(acac)_2$ solution was prepared in a vacuum system and measured in a sealed cell without exposure to air. It seems very probable that the low-energy band at 300 nm will not be observed for a dichloromethane solution containing no trace of water or other donor impurity. Thus, the 265 nm band may be concluded to be the only absorption by trimeric $Ni(acac)_2$ and the 300 nm band may be concluded to be caused by the donor impurity.

An aqueous solution of $Ni(acac)_2(H_2O)_2$ and a methanolic solution of $Ni(acac)_2(CH_3OH)_2$ both exhibit only one absorption maximum, at around 300 nm, with ε=21000 and 22000 respectively. In dry dichloromethane, however, both solvated complexes show the same spectra as that of the anhydrous trimer, indicating that the following trimerization equilibria are quickly attained and are favorable for the trimer under these conditions:

$$Ni(acac)_2L_2 \rightleftarrows \frac{1}{3}[Ni(acac)_2]_3 + 2L \quad (1)$$

The concentrations of the complexes, and hence of the coordinated solvents ($\sim10^{-5}$M), are nearly negligible compared to that of water ($\sim10^{-3}$M) contained *a priori* in dichloromethane. This situation seems to be the reason why $Ni(acac)_2(H_2O)_2$ and $Ni(acac)_2(CH_3OH)_2$ show no spectral difference from the anhydrous trimer. On the contrary, the spectrum of $Ni(acac)_2py_2$ in dichloromethane resembles that in methanol, showing an absorption band due to the acetylacetonate ligand only at 300 nm. It is thus certain that $Ni(acac)_2py_2$ is much more stable in dichloromethane and that Equilibrium (1) is favorable for the monomer adduct.

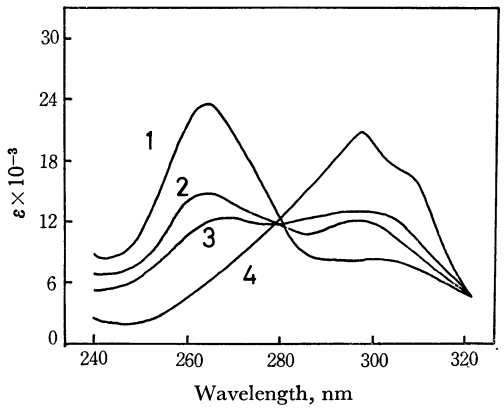

Fig. 2. Ultraviolet spectra of bis(acetylacetonato)nickel(II) in dichloromethane (curve 1), in dichloromethane containing methanol at the concentration of 1.2×10^{-2}M (curve 2) and 1.8×10^{-2}M (curve 3), and in methanol (curve 4). $[Ni(acac)_2]=1.776\times10^{-5}$M.

As is illustrated in Fig. 2, the peak-height ratio of the 265 and 300 nm bands decreases with an increase in methanol added to the dichloromethane solution of $Ni(acac)_2$, showing a gradual shift of Equilibrium (2)

$$Ni_3(acac)_6 + 6CH_3OH \rightleftarrows 3Ni(acac)_2(CH_3OH)_2 \quad (2)$$

$$K = \frac{[Ni(acac)_2(CH_3OH)_2]^3}{[Ni_3(acac)_6][CH_3OH]^6} \quad (3)$$

to the monomer side. Unfortunately, no absorption data in dichloromethane completely free from water are available, and so the determination of the equilibrium constant (3) is not possible. However, the concentrations of the trimer and the monomer are comparable, both lying in the region of 10^{-5}M when $\sim10^{-2}$M methanol is involved in dichloromethane. We can thus estimate K to be in the order of magnitude of 10^2M^{-4}.

Fackler[11] found that the reaction of bis(acetylacetonato)nickel(II) with pyridine in benzene proceeds *via* the intermediate $Ni_2(acac)_4py$, and estimated the equilibrium constants for the two steps by the spectrophotometric method:

$$2Ni_3(acac)_6 + 3py \rightleftarrows 3Ni_2(acac)_4py,$$

$$K_1 = \frac{[Ni_2(acac)_4py]^3}{[Ni_3(acac)_6]^2[py]^3} = ca.\ 10^{10}\ M^{-2}$$

11) J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **84**, 24 (1962).

$$Ni_2(acac)_4py + 3py \rightleftarrows 2Ni(acac)_2py_2,$$

$$K_2 = \frac{[Ni(acac)_2py_2]^2}{[Ni_2(acac)_4py][py]^3} = 2.7\times10^5\ M^{-2}$$

From these data, the equilibrium constant for the overall reaction (Eq. 4) is calculated to be $K=(K_1K_2^3)^{1/2}=ca.\ 10^{13}M^{-4}$:

$$Ni_3(acac)_6 + 6py \rightleftarrows 3Ni(acac)_2py_2 \qquad (4)$$

This value is very much larger than that (3) for the methanol adduct, conforming to the qualitative observation that $Ni(acac)_2py_2$ is quite stable and does not dissociate in dichloromethane.

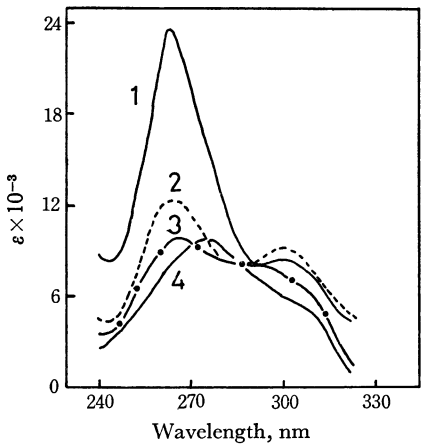

Fig. 3. Ultraviolet spectra of bis(acetylacetonato)nickel (II) in dichloromethane containing 4.54×10^{-3}M water at 10 min (curve 1), 1 hr (curve 2), 8 hr (curve 3) and 48 hr (curve 4) after dissolution.

The Hydrolysis Reaction of $Ni(acac)_2$ in Dichloromethane. Figure 3 represents the change with time of the ultraviolet spectra of $Ni(acac)_2$ in dichloromethane containing 4.54×10^{-3}M water. One hour after the dissolution, the high-energy peak was quite remarkably diminished, and it continued to decrease further with time. A new band gradually appeared in turn at 274 nm. Solutions of $Ni(acac)_2(H_2O)_2$ and $Ni(acac)_2(CH_3OH)_2$ in dry dichloromethane showed quite the same spectral change. When dichloromethane saturated with water (0.12M) was employed as the solvent, the 265 nm peak was not observed, but the 274 nm band appeared from the outset. The band position coincides with that of free acetylacetone, and suggests the occurrence of some hydrolytic reaction of $Ni(acac)_2$, thus liberating acetylacetone molecules. To confirm this possibility, a $Ni(acac)_2$ solution in dry dichloromethane was kept standing for 48 hr (Curve 4 in Fig. 3); the solvent was then distilled under reduced pressure. Acetylacetone in the distillate corresponded to 34.4% of the entire ligand.

In order to investigate the other hydrolysis product, a $Ni(acac)_2$ solution in water-saturated dichloromethane was kept standing for five days. A white, fuzzy precipitate resulted. The solvent was distilled under reduced pressure, and the residue was repeatedly washed with dichloromethane and then dried. This compound was soluble in methanol and exhibited the spectrum as shown by Curve 1 in Fig. 4. The yield of the compound was so minute that elemental analysis and other

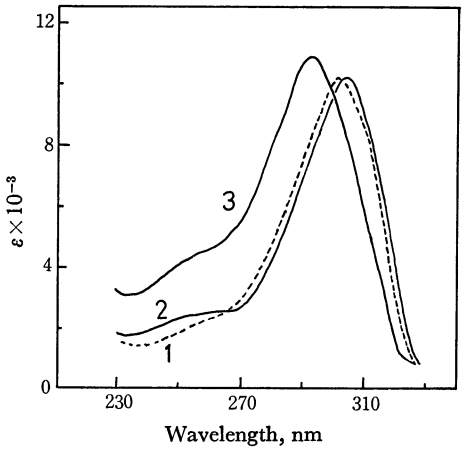

Fig. 4. Ultraviolet spectra in methanol of the hydrolysis product of bis(acetylacetonato)nickel(II) in dichloromethane (curve 1), $Ni(acac)(OH)(H_2O)_2$ (curve 2) and $[Ni(acac)(OCH_3)(CH_3OH)]_4$ (curve 3).

physical measurements were not possible, so a model compound was prepared for comparison.

Bertrand and his co-laborators synthesized a green compound $Ni(acac)(OCH_3)(CH_3OH)$ by the reaction of $Ni(acac)_2$ with equimolar potassium hydroxide in refluxing methanol.[9] The compound is tetrameric in chloroform and isostructural with $[Co(acac)(OCH_3)(CH_3OH)]_4$, which was shown by X-ray analysis to have a cubane-type structure.[12] The ultraviolet and infrared spectra of $[Ni(acac)(OCH_3)(CH_3OH)]_4$ were measured; they are shown in Figs. 4 and 5 respectively. As has been described in the Experimental section, an analogous hydroxo compound was prepared by the reaction of $Ni(acac)_2$ with potassium hydroxide in water. This compound, $Ni(acac)(OH)(H_2O)_2$, retains two molecules of solvent per nickel atom, and exhibits a very broad band in the O–H stretching region (Curve 1 in Fig. 5), a band which is sharpened by heating at

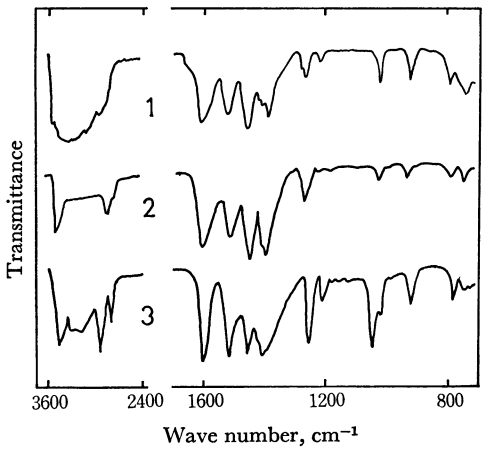

Fig. 5. Infrared spectra in Nujol (lower-frequency region) and in hexachlorobutadiene (higher-frequency region) of $Ni(acac)(OH)(H_2O)_2$ (curve 1), the same compound after heating at 100°C *in vacuo* (curve 2) and $[Ni(acac)(OCH_3)(CH_3OH)]_4$ (curve 3).

12) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **10**, 240 (1971).

100°C *in vacuo* (Curve 2 in Fig. 5). The infrared spectrum of $Ni(acac)(OH)(H_2O)_2$ bears a close resemblance to that of $[Ni(acac)(OCH_3)(CH_3OH)]_4$, and the former might also have a tetrameric structure similar to that of the latter, involving an excess H_2O molecule as the water of crystallization.

In Fig. 4 are reproduced the ultraviolet spectra of the tetrameric methoxo complex (Curve 2) and the presumably tetrameric hydroxo complex (Curve 3). They are very similar except that the latter is located in a little longer wavelength region than the former. It should be noted that the spectrum of the hydrolysis product of $Ni(acac)_2$ in dichloromethane (Curve 1) shows a striking resemblance to that of the synthesized hydroxo complex (Curve 2), suggesting an essential similarity between their structures.

If the hydrolysis of Ni $(acac)_2$ in dichloromethane proceeds according to Eq. (5), the yield of the freed acetylacetone will be 50% of the total acetylacetone contained in the starting complex. Cotton and

$$Ni_3(acac)_6 + 3nH_2O = \frac{3}{4}[Ni(acac)(OH)(H_2O)_{n-1}]_4 + 3acacH \quad (5)$$

Winquist[13] prepared a hexameric complex, $Ni_6(tfac)_{10}(OH)_2(H_2O)_2$ by drying a light green solid, presumably $Ni(tfac)_2(H_2O)_2$, at 108°C *in vacuo* for 24 hr; the solid had been obtained by a reaction between nickel(II) carbonate and trifluoroacetylacetone in refluxing benzene. If a similar hexameric complex is derived from $Ni(acac)_2$ in the present case, the yield of the freed acetylacetone will be 16.7%.

The observed yield of acetylacetone (34.4%) is higher than the value calculated for the above hexameric product (16.7%) and lower than that for the tetrameric product (50%). Although the tetrameric formulation seems preferable on the spectral basis, further detailed studies are desirable in order to establish the structure of the hydrolysis product of $Ni(acac)_2$ in dichloromethane.

The mechanism of the hydrolysis of bis(acetylacetonato)nickel(II) in dichloromethane containing more or less water is not certain as yet. However, it seems quite probable that the hydrolysis reaction of $Ni(acac)_2$ liberating an acetylacetone molecule does not proceed *via* $Ni(acac)_2(H_2O)_2$. If this is the case, the 300 nm band should rise with time at the expense of the 265 nm band. The observed results in Fig. 3 clearly obviate this possibility. Even when $Ni(acac)_2(H_2O)_2$ was dissolved in dichloromethane containing 4.54×10^{-3}M water, the spectrum was the same as that of a solution of anhydrous $Ni(acac)_2$, indicating a trimerization according to Eq. (1), and then it changed with time in the same fashion as shown in Fig. 3. Thus, the hydrolysis reaction of $Ni(acac)_2$ in question can be considered to start from the trimeric molecule.

The authors are grateful to the Ministry of Education for its financial assistance and also to the Daicel Co., Ltd. for the supply of acetylacetone.

13) F.A. Cotton and B.H.C. Winquist, *Inorg. Chem.*, **8**, 1304 (1969).