The Infrared Spectra of O-Deuterated and O-Methylated Derivatives of Diacetyl Monoxime and Isonitrosoacetone

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In a previous study the assignement of the absorption bands of diacetyl monoxime and isonitrosoacetone was carried out to determine the characteristic frequencies of the O=C–C=N system and also those of the functional group of oximes, –C=N–OH[1]. We have found that (1) these oximes take not a nitroso form but an oxime form in solutions; (2) the C=N stretching vibration appears in a lower frequency range than that of unconjugated oximes; (3) the oximes in solutions make intermolecular hydrogen bonds of an –O–H···O=C[*1] type, while unconjugated oximes in solutions or in the solid state make intermolecular hydrogen bonds of an –O–H···N=C type, and (4) the bond character of an O=C–C=N–OH system changes with the hydrogen bonding so that molecules in the free and in the associated state have two sets of frequencies corresponding to these states. The characteristic frequencies of C=N bonds have been observed for some kinds of compounds, such as unconjugated imines[2], unconjugated

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[*1] Measurements of the dipole moments also rule out intramolecular association (unpublished work).

[2] P. L. Pickard and G. W. Polly, *J. Am. Chem. Soc.*, 76, 5169 (1954).

oximes[3-7], conjugated imines[8], conjugated oximes containing phenyl groups[9,10], azines[11], glyoximes[12] and so on[13]. It is worth noting that the frequencies of the bands scatter over a very wide range of wave numbers, 1520~1680 cm^{-1}, depending on the kinds of compounds or the existence of hydrogen bonding. Moreover, absorption intensity is affected to a considerable extent by the environment around a C=N bond[13,14]. Now that the assignment of bands has been made for diacetyl monoxime and isonitrosoacetone, it is quite interesting to observe the effect of environments on the infrared spectra of the O=C–C=N–OH system. Therefore, the *O*-deuterated and *O*-methylated derivatives of diacetyl monoxime and isonitrosoacetone have been dealt with in the present study in order to investigate the effect of substituents on the positions and intensities of bands of the O=C–C=N–O system. This study will also serve to confirm the previous assignment. When the Raman and infrared spectra of these oximes were reported on by Kahovec and Kohlrausch[15], Matsui[16] and Milone and Borello[17], they were not completely analyzed.

Experimental

Deuterated samples were prepared from the same purified samples as used in the previous study[1] by exchanging the hydrogen in OH groups with deuterium in heavy water. These samples were dried before use.

Commercial preparations of diacetyl monoxime-*O*-methyl ether and isonitrosoacetone-*O*-methyl ether were purified by distillation under atmospheric and reduced pressure respectively.

The spectra were taken with the optical system of a Hilger H-800 spectrophotometer equipped with interchangeable fluorite and rock-salt prisms. Solutions of various concentrations in carbon tetrachloride, carbon disulfide and chloroform were

TABLE I. OBSERVED FREQUENCIES (cm^{-1}) OF DIACETYL MONOXIME AND DIACETYL MONOXIME-*d**

-C=N-OH		-C=N-OD		Intensity change on dilution	Assignment**
Solution	Solid	Solution	Solid		
3577				Increase	$\nu(\mathrm{OH})_{\mathrm{free}}$
3345	~3250 (s, b)			Decrease	$\nu(\mathrm{OH})_{\mathrm{assoc}}$
		2630		Increase	$\nu(\mathrm{OD})_{\mathrm{free}}$
		~2420	2425 (s, b)	Decrease	$\nu(\mathrm{OD})_{\mathrm{assoc}}$
1698		1696		Increase	$\nu(\mathrm{C=O})_{\mathrm{free}}$
1686	1665 (vs)	1688	1664 (vs)	Decrease	$\nu(\mathrm{C=O})_{\mathrm{assoc}}$
1630 (w)		1619 (m)	1610 (m)		$\nu(\mathrm{C=N})$
	~1450 (m)			Decrease	$\delta(\mathrm{OH})_{\mathrm{in\text{-}plane,\ assoc}}$
1424 (m)	~1420 (m)	1424 (m)	1418 (m)		$\delta(\mathrm{CH_3})_{\mathrm{deg}}$
1365 (s)	1365 (s)	1362 (s)	1366 (s)		$\delta(\mathrm{CH_3})_{\mathrm{sym}}$
1355				Increase	$\delta(\mathrm{OH})_{\mathrm{in\text{-}plane,\ free}}$
1301 (w)	1313 (w)	1306 (w)	1313 (w)		$\nu(\mathrm{C\text{-}C})_{\mathrm{central}}$
1124 (s)	1125 (s)	1124 (s)	1134 (m)		$\rho(\mathrm{N=C\text{-}CH_3})_{\mathrm{in\text{-}plane}}$
		~1080	1090 (m)	Decrease	$\delta(\mathrm{OD})_{\mathrm{in\text{-}plane,\ assoc}}$
1022 (s)	~1020 (s)	1017 (s)	~1015 (s)		$\rho(\mathrm{O=C\text{-}CH_3})_{\mathrm{in\text{-}plane}}$
		995		Increase	$\delta(\mathrm{OD})_{\mathrm{in\text{-}plane,\ free}}$
970	980 (m)	970	~ 975 (m)	Decrease	$\nu(\mathrm{N\text{-}O})_{\mathrm{assoc}}$
963				Increase	$\nu(\mathrm{N\text{-}O})_{\mathrm{free}}$
933 (w)	933 (w)	930 (w)	933 (w)		$\nu(\mathrm{C\text{-}CH_3})$

* Frequencies to be assigned to the C–H stretching vibrations are not listed in this table.

** ν, stretching; δ, bending; ρ, rocking

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TABLE II. OBSERVED FREQUENCIES (cm^{-1}) OF ISONITROSOACETONE AND ISONITROSOACETONE-*d**

-C=N-OH		-C=N-OD		Intensity change on dilution	Assignment
Solution	Solid	Solution	Solid		
3574				Increase	$\nu(OH)_{free}$
3325				Decrease	$\nu(OH)_{assoc}$
		2620		Increase	$\nu(OD)_{free}$
		~2440		Decrease	$\nu(OD)_{assoc}$
1703		1696		Increase	$\nu(C{=}O)_{free}$
1674	1658 (vs)	1673	~1652 (vs)	Decrease	$\nu(C{=}O)_{assoc}$
1614 (w)	1620 (w)	1599 (m)	1581 (m)		$\nu(C{=}N)$
~1450	~1445 (m, b)	~1454	1447 (m, b)	Decrease	$\delta(OH)_{in\text{-}plane,\ assoc}$
$(1427)_{estimated}$					$\delta(CH_3)_{deg}$
1398				Increase	$\delta(OH)_{in\text{-}plane,\ free}$
1366 (s)	1372 (s)	1372 (s)	1377 (s)		$\delta(CH_3)_{sym}$
1320 (vw)	1307 (vw)	1321 (m)	1327 (m)		$\nu(C\text{-}C)_{central}$
1226 (m)	1240 (m)	1223 (m)	1245 (m)		$\delta(CH)_{in\text{-}plane}$
			1062	Decrease	$\delta(OD)_{in\text{-}plane,\ assoc}$
1016	1015 (s)	1015	1017 (s)	Increase	$\delta(OD)_{in\text{-}plane,\ free}$ $\rho(O{=}C\text{-}CH_3)_{in\text{-}plane}$
990	991 (m)	990	988 (m)	Decrease	$\nu(N\text{-}O)_{assoc}$
972		971		Increase	$\nu(N\text{-}O)_{free}$
920 (m)	~ 929 (m)	918 (m)	921 (m)		$\nu(C\text{-}CH_3)$
835 (w)	850 (w)	831 (w)	848 (w)		$\delta(CH)_{out\text{-}of\text{-}plane}$

* Frequencies to be assigned to the C-H stretching vibrations are not listed in this table.

TABLE III. OBSERVED FREQUENCIES (cm^{-1}) OF DIACETYL MONOXIME- AND ISONITROSO-ACETONE-*O*-METHYL ETHERS*

Diacetyl monoxime-*O*-methyl ether	Isonitroso-acetone-*O*-methyl ether	Assignment
1695 (vs)	1696 (vs)	$\nu(C{=}O)$
1610 (s)	1588 (m)	$\nu(C{=}N)$
1463 (m)	1465 (m)	$\delta(O\text{-}CH_3)_{deg}$
1442 (m)	1446 (m)	$\delta(O\text{-}CH_3)_{sym}$
1428 (m)	1427 (m)	$\delta(C\text{-}CH_3)_{deg}$
1361 (vs)	1367 (s)	$\delta(C\text{-}CH_3)_{sym}$
1311 (s)	1318 (m)	$\nu(C\text{-}C)_{central}$
	1236 (m)	$\delta(CH)_{in\text{-}plane}$
1190 (vw)	1180 (w)	$\rho(N\text{-}O\text{-}CH_3)_{in\text{-}plane}$
1124 (vs)		$\rho(N{=}C\text{-}CH_3)_{in\text{-}plane}$
1049 (vs)	1052 (s)	$\nu(N\text{-}O\text{-}C)_{antisym}$
1011 (sh)	1007 (m)	$\rho(O{=}C\text{-}CH_3)_{in\text{-}plane}$
945 (sh) 917 (s)	918 (m)	$\nu(C\text{-}CH_3)$ $\nu(N\text{-}O\text{-}C)_{sym}$
	830 (w)	$\delta(CH)_{out\text{-}of\text{-}plane}$

* Frequencies to be assigned to the C-H stretching vibrations are not listed in this table.

used in order to observe changes in the absorption intensity with changes in the concentration. Isonitrosoacetone-*d* was used only in dilute solutions, since it has only a limited solubility in the solvents used. The deuterated oximes in the solid state were examined as mulls in Nujol and hexachlorobutadiene. The methylated oximes in the liquid state were also examined. However, no additional data were obtained.

The observed frequencies of absorption bands are listed in Tables I, II and III. For the sake of comparison, the observed frequencies of the original oximes are also included in Tables I and II. These values are reproduced from the previous paper[1]. However, the C-H stretching frequencies are omitted from the tables, because they are not necessary for later discussion. Some portions of the spectra are shown in Figs. 1 to 9.

Assignment and Discussion

The Stretching Frequencies of O=C-C=N.— The bands previously assigned to the C=O stretching vibrations, $\nu(C{=}O)$, of diacetyl monoxime and isonitrosoacetone show no appreciable change in their positions and intensities on deuteration. The general behavior of the concentration dependence of the intensity is also unaltered by replacing hydrogen with deuterium. However, the $\nu(C{=}O)$ bands of associated molecules at 1686 cm^{-1} for diacetyl monoxime and at 1674 cm^{-1} for isonitrosoacetone not only become weak on dilution but also disappear on methylation (Figs. 1 and 2). These facts confirm the previous assignment. The vibrational mode in the solid state absorbs at a frequency lower by about 20 cm^{-1} than that in solution. The low-frequency shift is a quite general phenomenon observed in condensed phases.

For the C=N stretching vibration, $\nu(C{=}N)$, distinct variations in intensity and position are observed on deuteration and methylation.

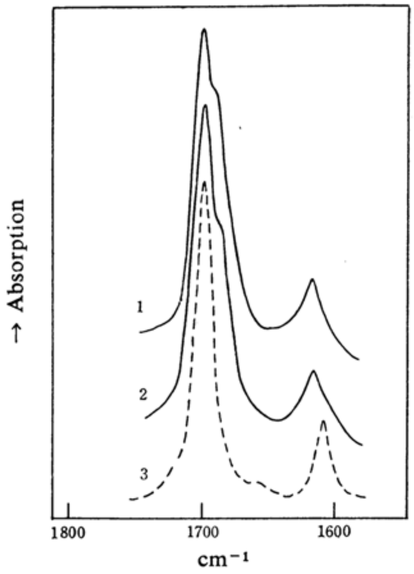

Fig. 1. Infrared spectra of diacetyl monoxime-*d* in CCl_4 solutions: (1) 0.148 mol./l., 0.2 mm. cell; (2) 0.059 mol./l., 0.5 mm. cell, and (3) diacetyl monoxime-*O*-methyl ether (liq.).

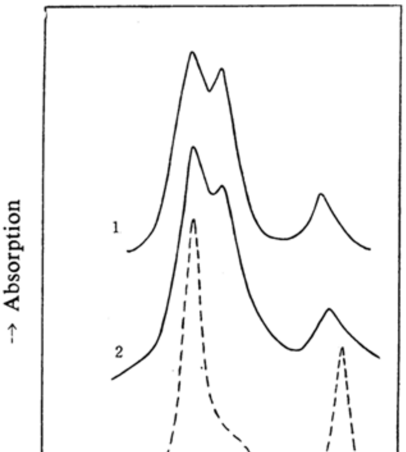

Fig. 2. Infrared spectra of isonitrosoacetone-*d* in $CHCl_3$ solutions: (1) 0.515 mol./l., 0.05 mm. cell; (2) 0.130 mol./l., 0.2 mm. cell, and (3) isonitrosoacetone-*O*-methyl ether (liq.).

Deuteration gives rise to a lowering in frequency along with a slight but perceptible increase in intensity. Methylation causes a similar frequency shift and an intensity change, the magnitude of which is, however, much greater than that on deuteration (Figs. 1 and 2). As a result, the methylated oximes have rather strong and sharp ν(C=N) bands, unlike the original oximes. The doubling of the ν(C=N) bands attributable to free and associated molecules could not be detected for either the deuterated compounds or the original compounds. This fact suggests that the influence of association does not practically extend to the C=N bonds. The ν(C=N) band of diacetyl monoxime in the solid state is masked by the strong band of ν(C=O).

For all compounds treated in the present study, the C=O stretching vibrations appear in a region of lower frequency than that of unconjugated ketones (1705∼1725 cm^{-1})13), while the frequencies of the C=N stretching vibrations are lower than those of unconjugated oximes or imines (1660∼1680 cm^{-1}). Conjugation in an O=C–C=N system is considered to be the cause of the lowering in the ν(C=O) and ν(C=N) frequencies. We can find the following absorption ranges for ν(C=O)13,18): α-diketones, 1710∼1730 cm^{-1}; α,β-unsaturated ketones, 1665∼1685 cm^{-1}; and for ν(C=N): azines11), about 1660 cm^{-1}; benzaldoximes8,13), 1620∼1660 cm^{-1}. Thus, ν(C=O) in an O=C–C=N system can be considered to absorb in a wave number range between those of saturated ketones and of α,β-unsaturated ketones. The ν(C=N) is in a wave number range still lower than that of a C=N group conjugated with a phenyl group[*2]. *vic*-Dioximes appear to have very weak absorptions near 1620 cm^{-1} originating from an N=C–C=N system19)[*3]. This value is very close to the ν(C=N) wave number in an O=C–C=N system.

Deuteration and methylation result in an increase in absorption intensity and a decrease in frequency for ν(C=N), but not for ν(C=O). The frequency shift of ν(C=N) is probably a natural consequence of substitution. The fact that there is no significant change in ν(C=O) implies that the substitution does not affect the C=O bond.

As Cross and Rolfe have pointed out5), the C=N absorption intensities of oximes are generally weak, while those of other kinds of compounds are not necessarily so. Once the hydrogen atom of an OH group is replaced by another atom or group, the C=N absorption band is intensified. Matsui also made a similar

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18) See also M. L. Josien, J. Lascombe, J. Lecomte and J. P. Mathieu, *Compt. rend.*, **240**, 1982 (1955).

[*2] Palm and Werbin reported the value of about 1620 cm^{-1} for the ν(C=N) of α-benzaldoxime9). As the value was observed in the solid state, the frequency for a free state is possibly higher than this.

[*3] The frequency was estimated from the spectra given by Voter et al. in their paper19).

19) R. C. Voter, C. V. Banks, V. A. Fassel and P. W. Kehres, *Anal. Chem.*, **23**, 1730 (1951).

finding in his studies of oximes[16]. This seems to be characteristic of the spectra of oximes.

Hydrogen bonding gives rise to a shift towards a frequency lower by about 10 cm^{-1} for the ν(C=O) of diacetyl monoxime and by about 25 cm^{-1} for that of isonitrosoacetone. In general, a frequency shift caused by hydrogen bonding does not exceed 10 cm^{-1} in unconjugated ketones[20,21]. The frequency shift in diacetyl monoxime is of the same order as that in unconjugated ketones. On the other hand, the frequency shift in isonitrosoacetone is greater than that in unconjugated ketones.

In the previous paper, the bands due to the C–C stretching vibrations, ν(C–C)$_{\text{central}}$, in the system discussed here were placed near 1300 cm^{-1} for diacetyl monoxime and at 1320 cm^{-1} for isonitrosoacetone. The corresponding bands of deuterated oximes are at 1306 and 1321 cm^{-1}, while those of methylated oximes are at 1311 and 1318 cm^{-1}. The bands of these oximes become intense on deuteration and more intense on methylation (Figs. 3—6). This property of ν(C–C)$_{\text{central}}$ is analogous to that of ν(C=N). The bands of the deuterated oximes look like single bands rather than composite ones. Reexamination of diacetyl monoxime revealed that two well-defined bands and their concentration dependence could not always be observed. Accordingly, only one frequency is shown in Table I for the ν(C–C)$_{\text{central}}$ of diacetyl monoxime.

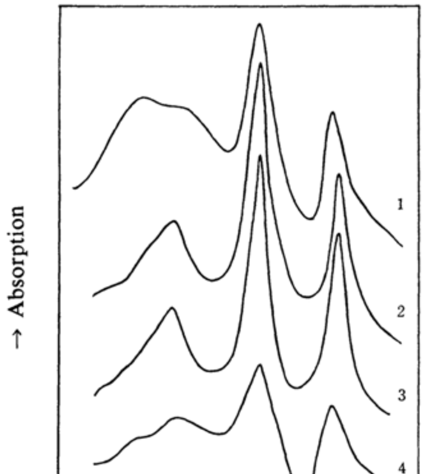

Fig. 3. Infrared spectra of (1) diacetyl monoxime in hexachlorobutadiene mull; and the spectra of diacetyl monoxime-*d* (2) in CCl$_4$, 0.059 mol./l., 0.5 mm. cell; (3) in CCl$_4$, 0.148 mol./l., 0.2 mm. cell, and (4) in hexachlorobutadiene mull.

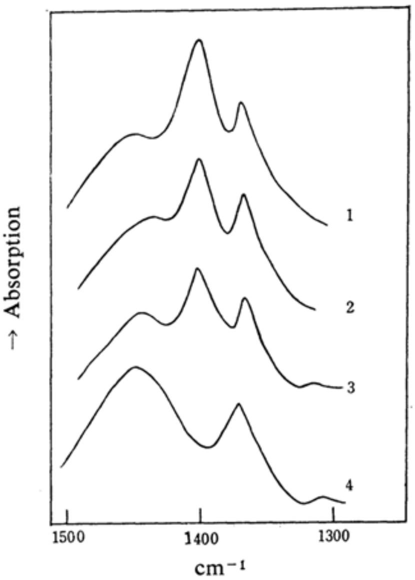

Fig. 4. Infrared spectra of isonitrosoacetone (1) in CHCl$_3$, 0.125 mol./l., 0.2 mm. cell; (2) in CHCl$_3$, 0.250 mol./l., 0.1 mm. cell; (3) in CHCl$_3$, 0.500 mol./l., 0.05 mm. cell, and (4) in KBr disk.

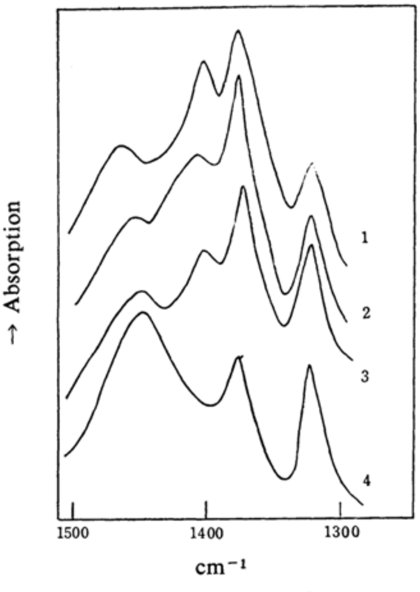

Fig. 5. Infrared spectra of isonitrosoacetone-*d* (1) in CHCl$_3$, 0.125 mol./l., 0.2 mm. cell; (2) in CHCl$_3$, 0.250 mol./l., 0.1 mm. cell; (3) in CHCl$_3$, 0.500 mol./l., 0.05 mm. cell, and (4) in hexachlorobutadiene mull.

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[20] R. S. Rasmussen, D. D, Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

[21] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, **1951**, 877.

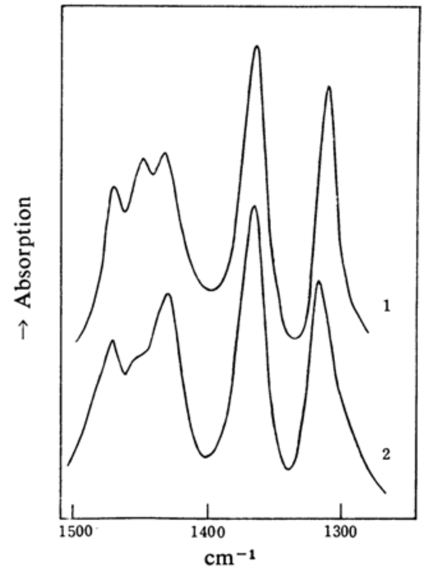

Fig. 6. Infrared spectra of (1) diacetyl monoxime-*O*-methyl ether (liq.), and (2) isonitrosoacetone-*O*-methyl ether (liq.).

The Stretching Frequencies of N–O and N–O–C.—In the previous study, the bands of diacetyl monoxime at 970 and 963 cm^{-1} and of isonitrosoacetone at 990 and 972 cm^{-1} were assigned to the N–O stretching vibrations, ν(N–O).

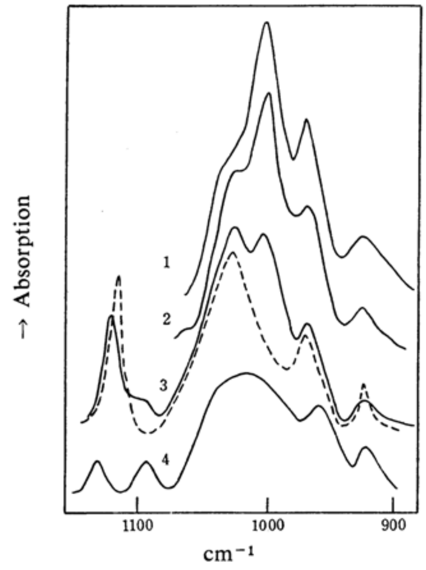

Fig. 7. Infrared spectra of diacetyl monoxime-*d* (1) in CS_2, 0.02 mol./l., 1.5 mm. cell; (2) in CS_2, 0.059 mol./l., 0.5 mm. cell; (3) in CCl_4, 0.345 mol./l., 0.085 mm. cell, and (4) in hexachlorobutadiene mull. The dotted line indicates the spectrum of diacetyl monoxime in CCl_4 at the same concentration as (3).

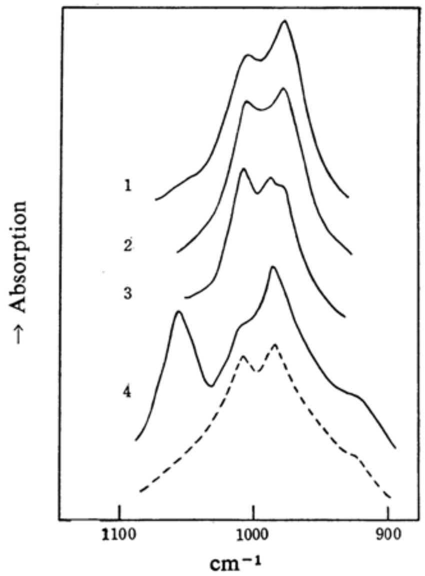

Fig. 8. Infrared spectra of isonitrosoacetone-*d* (1) in $CHCl_3$, 0.13 mol./l., 0.2 mm. cell; (2) in $CHCl_3$, 0.26 mol./l., 0.1 mm. cell; (3) in $CHCl_3$, 0.52 mol./l., 0.05 mm. cell, and (4) in Nujol mull. The dotted line indicates the spectrum of isonitrosoacetone in Nujol mull.

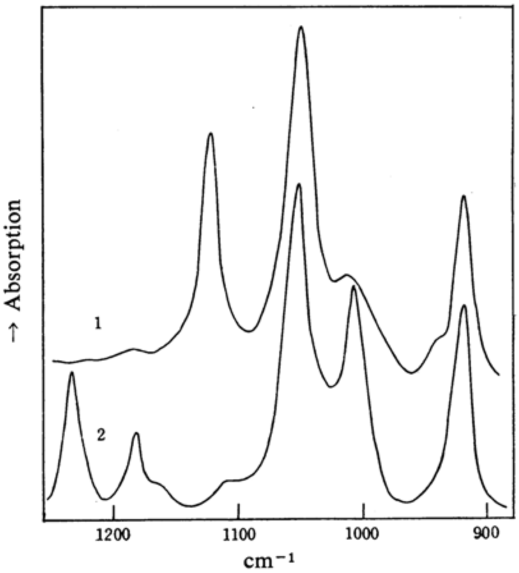

Fig. 9. Infrared spectra of (1) diacetyl monoxime-*O*-methyl ether (liq.), and (2) isonitrosoacetone-*O*-methyl ether (liq.).

On deuteration, no appreciable changes can be observed in the absorption frequencies and in the concentration dependence of the intensity (Figs. 7 and 8). The N–O stretching frequencies of this type of oximes are higher than those of unconjugated oximes[3,7–9] or benzaldoxime[22], but lower than that of benzoquinone monoxime[10]. This difference in characteristic frequencies is possibly due to the double-bond characters of N–O bonds in conjugation with adjacent bonds or groups as has been stated above.

The bands mentioned above, however, must be turned into an entirely different pattern by methylation, because an N–O system is replaced by a system of three atoms, N–O–C. As expected, all the N–O stretching bands of oximes are missing in the spectra of methyl ethers. Instead, new bands appear at 1190, 1049 and 917 cm^{-1} for diacetyl monoxime-*O*-methyl ether and 1180 and 1052 cm^{-1} for isonitrosoacetone-*O*-methyl ether (Fig. 9). Strong bands are to be assigned to the N–O–C stretching vibration, ν(N–O–C), while weak bands are to be assigned to the CH_3 rocking vibration, as is described below. The stretching vibration of a C–O–C system in alkyl ethers[13] absorbs in the 1060∼1150 cm^{-1} range. Analyzing the spectra of dimethyl ether, Kanazawa and Nukada assigned a band at 928 cm^{-1} to the symmetric stretching vibration and a band at 1102 cm^{-1} to the antisymmetric vibration of C–O–C[23]. Accordingly, two strong bands at 1049 and 917 cm^{-1} for diacetyl monoxime-*O*-methyl ether can be assigned to ν(N–O–C). The corresponding bands of isonitrosoacetone-*O*-methyl ether are a band at 1052 cm^{-1} and perhaps a band at 918 cm^{-1} (Figs. 8 and 9). Although the band at 918 cm^{-1} is not a band appearing only in the case of *O*-methylated isonitrosoacetone, it is strengthened by substituting a methyl group for hydrogen. Therefore, it seems to be much more reasonable to assign the band at 918 cm^{-1} rather than a weak band at 1180 cm^{-1} to ν(N–O–C). A value of 918 cm^{-1} for *O*-methylated isonitrosoacetone is practically equal to the value of 917 cm^{-1} for *O*-methylated diacetyl monoxime. The bands near 1050 cm^{-1} are stronger than those near 918 cm^{-1}. The formers belong to the antisymmetric vibration, and the latters, to the symmetric vibration of the N–O–C.

The Stretching and Bending Frequencies of OH and OD.—The bands representing the OD stretching vibration, ν(OD), are evidently those at 2630 and 2420 cm^{-1} for diacetyl monoxime-*d* and those at 2620 and 2440 cm^{-1} for isonitrosoacetone-*d*. In the solid state only bands near 2400 cm^{-1} appear. The observed frequencies of these bands were roughly estimated because of the disturbance caused by the absorption of carbon dioxide. The ν(OD) bands completely disappear from the spectra of the methylated oximes. The bands near 2600 cm^{-1} should be assigned to the ν(OD) of free molecules, and the bands near 2400 cm^{-1}, to that of associated molecules. The values of the ν(OH) : ν(OD) frequency ratio are 1.36 and 1.38 for the free and the associated state of diacetyl monoxime and 1.36 for both states of isonitrosoacetone.

In the previous study, the band of diacetyl monoxime at 1355 cm^{-1} and that of isonitrosoacetone at 1398 cm^{-1} were assigned to the OH in-plane bending vibration, $\delta(\mathrm{OH})_{\text{in-plane}}$, of free molecules. These bands disappear on deuteration (Figs. 3—6). Therefore, the assignment made in the previous study is justified. New bands of free molecules attributable to the OD in-plane bending vibration, $\delta(\mathrm{OD})_{\text{in-plane}}$, appear at 995 cm^{-1} for diacetyl monoxime-*d* and near 1015 cm^{-1} for isonitrosoacetone-*d* in solution. The former band becomes strong with a decrease in the concentration. The concentration dependence of the latter is not simple (Figs. 7 and 8). Judging from the complicated appearance of the band, it can hardly be regarded as a single absorption band. The band changes into a sharp band on methylation (Fig. 9). Therefore, it can be considered to be a composite band of $\delta(\mathrm{OD})_{\text{in-plane}}$ and the rocking vibration of CH_3 attached to the C=O group of isonitrosoacetone-*d*. The values of the δ(OH) : δ(OD) frequency ratio are 1.36 and 1.38 for diacetyl monoxime and isonitrosoacetone respectively.

The $\delta(\mathrm{OH})_{\text{in-plane}}$ band of diacetyl monoxime in the associated state could not be determined definitely in the previous study owing to an overlap with a band at 1424 cm^{-1}. The present study revealed that in solutions a band in this region becomes relatively sharp on deuteration and even sharper on methylation. The corresponding band in the solid state is a broad one at 1450 cm^{-1} which disappears on deuteration (Fig. 3). From these facts, the band at 1450 cm^{-1} can be considered to represent the $\delta(\mathrm{OH})_{\text{in-plane}}$ of diacetyl monoxime in the associated state. Even in solutions, the band should be considered to be present near 1450 cm^{-1}, although it cannot be located precisely because of the presence of a band at 1424 cm^{-1}.

For isonitrosoacetone, no definite conclusion could be drawn in the present study about the exact position of the $\delta(\mathrm{OH})_{\text{in-plane}}$ in the associated state. Nevertheless, it is most likely that the band near 1450 cm^{-1} arises from the δ(OH) of isonitrosoacetone in the associated state and that the CH_3 degenerate deformation band overlaps the band (Fig. 4).

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[22] A. Palm and H. Werbin, *Can. J. Chem.*, 32, 858 (1954).

[23] Y. Kanazawa and K. Nukada, This Bulletin, 35, 612 (1962). See also Y. Masiko, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 79, 470 (1958).

A very weak band at about 1080 cm^{-1} can be assigned to the $\delta(OD)_{in\text{-}plane}$ of associated diacetyl monoxime-*d*, since it becomes more intense at higher concentrations. In the solid state, two bands appear at 1090 and 1134 cm^{-1} in place of a very weak band at about 1080 cm^{-1} and a strong band at 1124 cm^{-1} in solution (Fig. 7). A band at 1124 cm^{-1} is assigned to the CH_3 rocking vibration in N=C–CH_3, $\rho(N=C-CH_3)$, below. The two bands in the spectrum of the solid have nearly equal intensities and are only half as intense as the band at 1124 cm^{-1} in solution. The frequency shifts and the intensity changes arise probably from a coupling between δ(OD) and $\rho(N=C-CH_3)$ in the associated state. In solution it seems that the band at 1134 cm^{-1}, due to relatively few associated molecules, is poorly defined because of the existence of the strong band at 1124 cm^{-1} due to free molecules (Fig. 7).

The band of solid isonitrosoacetone-*d* at 1062 cm^{-1} can be assigned to the δ(OD) in association, although no distinct band was detected near 1062 cm^{-1} in the spectra of solutions since concentrated solutions could not be prepared. The values of the $\delta(OH):\delta(OD)$ frequency ratio are 1.33 for diacetyl monoxime and 1.36 for isonitrosoacetone.

The Bending and Rocking Vibrations of CH_3 and CH.—The bands at 1424 and 1365 cm^{-1} and those at 1450 and 1366 cm^{-1} were assigned previously to the CH_3 deformation vibrations of diacetyl monoxime and isonitrosoacetone respectively[1]. The assignment of the 1450 cm^{-1} band, however, was somewhat ambiguous. The corresponding bands of the deuterated oximes are the bands at 1424 and 1362 cm^{-1} for diacetyl monoxime-*d* and those at about 1465 and 1372 cm^{-1} for isonitrosoacetone-*d*.

Their methyl ethers show bands at 1463, 1442, 1428 and 1361 cm^{-1} for diacetyl monoxime-*O*-methyl ether and bands at 1465, 1446, 1427 and 1367 cm^{-1} for isonitrosoacetone-*O*-methyl ether (Fig. 6). Two new bands observed in the spectra of the methyl ethers do not show the concentration dependence of the intensity. Among the four bands of diacetyl monoxime-*O*-methyl ether, the bands at 1424 and 1365 cm^{-1} can readily be assigned to the CH_3 deformation vibrations of C–CH_3, $\delta(C-CH_3)$, because they are present in the spectra of both the original and deuterated oximes. Therefore, the bands at 1463 and 1442 cm^{-1} should be attributed to the CH_3 deformation vibrations of O–CH_3, $\delta(O-CH_3)$. The band at 1463 cm^{-1} is stronger than that at 1442 cm^{-1}. The former represents the antisymmetric vibration, and the latter, the symmetric one.

For diacetyl monoxime no substantial change in the positions and intensities of the CH_3 deformation bands is produced by *O*-methylation. A band at about 1365 cm^{-1} is characteristic of all the compounds under investigation. Therefore, it is a natural inference that the CH_3 degenerate deformation vibrations of isonitrosoacetone and its deuterated compound will also give rise to bands at about 1427 cm^{-1}, corresponding to the band observed for the methyl ether, although the band was not identified on the spectrum of the oxime itself because of a broad band due to the $\delta(OH)_{in\text{-}plane}$. The remaining bands of isonitrosoacetone-*O*-methyl ether, at 1465 and 1446 cm^{-1}, should be assigned to $\delta(O-CH_3)_{degenerate}$ and $\delta(O-CH_3)_{symmetric}$ respectively. Thus, a consistent interpretation can be achieved for the CH_3 deformation bands. The values of 1465 and 1446 cm^{-1} for $\delta(O-CH_3)$ lie in the same range as that observed for dimethyl ether by Kanazawa and Nukada[23], these values being higher than those of $\delta(C-CH_3)$ in alkanes.

The band of isonitrosoacetone at 1226 cm^{-1} was assigned previously to the CH in-plane bending vibration, $\delta(CH)_{in\text{-}plane}$. The corresponding bands are present at 1223 cm^{-1} for its deuterated oxime and at 1236 cm^{-1} for its methyl ether. A band at 831 cm^{-1} for the deuterated and methylated isonitrosoacetone can be attributed to the CH out-of-plane bending vibration, $\delta(CH)_{out\text{-}of\text{-}plane}$. None of the bands discussed in this paragraph appear in the spectra of diacetyl monoxime and its derivatives.

There are bands at 1017 and at 1011 cm^{-1} for deuterated and methylated diacetyl monoxime respectively. Similarly, there are bands at 1015 and at 1007 cm^{-1} for deuterated and methylated isonitrosoacetone respectively. These bands are unequivocally due to the CH_3 in-plane rocking vibrations, $\rho(O=C-CH_3)$, of O=C–CH_3, which have bands at 1022 and 1016 cm^{-1} for the original oximes.

In addition, diacetyl monoxime and its derivatives have bands at exactly the same frequency, 1124 cm^{-1}. These bands must be due to the CH_3 in-plane rocking vibrations, $\rho(N=C-CH_3)$, of N=C–CH_3. These facts convince us of the correctness of the assignments made in the previous study. For the solid of diacetyl monoxime-*d*, the band at 1134 cm^{-1} may be interpreted as $\rho(N=C-CH_3)$. The position can be considered to shift in the solid state through a coupling with δ(OD), as has already been mentioned.

In methyl ethers, the CH_3 rocking vibration, $\rho(O-CH_3)$, of O–CH_3 should appear in the rock-salt region. With a methyl group in place of hydrogen, a new additional weak band appeared at 1190 cm^{-1} for diacetyl monoxime-*O*-methyl ether and at 1180 cm^{-1} for isonitrosoacetone-*O*-methyl ether. The weak band near 1190 cm^{-1} is assigned to $\rho(O-CH_3)$.

The bands of the deuterated diacetyl monoxime at 930 cm^{-1} and of the methylated one at 945 cm^{-1} correspond to the weak band of the original oxime at 933 cm^{-1} which was previously assigned to $\nu(C-CH_3)$. However, the band of the methyl ether at 945 cm^{-1} is detectable merely as a shoulder on the higher frequency side of a strong band at 917 cm^{-1}. Consequently, the observed frequency can only roughly be estimated. For isonitrosoacetone and its derivatives, the corresponding bands are weak ones at 920 cm^{-1} in the oxime and at 918 cm^{-1} in the deuterated and methylated oximes. It is most probable that these bands are due to the stretching vibrations of $C-CH_3$ bonds, $\nu(C-CH_3)$, because the C–C stretching bands cannot be considered to shift substantially on deuteration and methylation and also because no other bands could be found in the spectra of isonitrosoacetone.

Summary

The infrared absorption bands due to the O=C–C=N–OH system have been investigated by the use of diacetyl monoxime, isonitrosoacetone, and their *O*-deuterated and *O*-methylated derivatives. All the bands observed have been reasonably assigned. So far as the infrared spectra are concerned, the degree of conjugation in the C=O bonds is between those of saturated ketones and α, β-unsaturated ketones. The degree of conjugation in the C=N bonds is greater than those of conjugated imines and of aldoximes containing a C=C–C=N group and is approximately equal to those of *vic*-dioximes containing an N=C–C=N group. Under the influence of conjugation, the N–O bonds have a greater double-bond character than those of unconjugated oximes. The bond character varies with the hydrogen bonding, the type of which is not -O–H···N=C, but –O–H···O=C. In general, the bands due to the C=N bonds of oximes are weak. However, they are intensified by deuteration and are intensified remarkably by methylation.

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