Infrared Spectra of Acyclic Imides. IV. Effects of Alkali Halides on the Infrared Spectra of Diacetamide

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Anomalies in the infrared spectra of some polar molecules in the alkali halide disk technique have often been reported¹⁾. In case of benzoic acid²⁾, potassium iodide disks have been recommended to obtain the same infrared spectra as those of pastes. On the other hand, molecules containing the -CONHCO- group such as succinimide³⁾, cyanuric acid⁴⁾ and barbituric acid⁵⁾, have been reported to undergo spectral changes depending on the method of preparation of samples. In the present paper, we will report that diacetamide (CH_3-CONHCO-CH_3), which has been revealed to exhibit dimorphism⁶⁾, also shows an analogous anomaly. An inversion of configuration of the -CONHCO- group is suggested to take place in the course of this spectral change. The ionic radii of the anions and the cations of alkali halides involved as well as the amount of water contained in the sample have been proved to influence the spectral change. The effect of compression in the disk technique has also been examined.

Results and Discussion

Alkali Halide Anomaly and Dimorphism of Diacetamide. — The crystal of diacetamide in form A undergoes marked changes in infrared spectra on the addition of various alkali halides. This phenomenon was observed at first for potassium iodide, in the course of measurements in the disk technique. As reported in the preceding paper⁶⁾, diacetamide in form A shows two C=O stretching bands at 1734 and 1700 cm^{-1}, the stronger one being the band at 1700 cm^{-1}. This was always the case for Nujol or hexachlorobutadiene pastes. For potassium bromide disks however, both of these bands sometimes underwent changes in relative intensities so that the band at 1734 cm^{-1} became the stronger one. In an attempt to prevent this spectral change, the use of potassium iodide as the matrix²⁾ was made to result in a marked spectral change of different type over the whole region measured.

On the other hand, another crystal form (form B) was found for diacetamide⁶⁾ and a close similarity in infrared spectra was observed between pastes of the form B and potassium iodide disks of form A. Furthermore, form A and form B were proved to involve the trans-cis and the trans-trans -CONHCO- group respectively, giving rise to infrared spectra markedly different from each other. Thus, the above fact concerning potassium iodide suggests that the configuration of the -CONHCO- group is changed from the trans-cis to the trans-trans configuration in the course of preparation of potassium iodide disks from form A. To confirm this, further investigations with the use of various alkali halides have been made and the following results have been obtained.

Effects of Various Alkali Halides. — *1) Potassium Iodide, Sodium Iodide and Sodium Bromide.*—The presence of these alkali halides gives rise to analogous changes in infrared spectra of the form A of diacetamide not only in the disk technique but also in the paste method. Here, the paste method means the technique in which the mixture of diacetamide in form A and one of potassium iodide, sodium iodide and sodium bromide (the molar ratio being approximately one to one) is mulled with Nujol or hexachlorobutadiene. It is seen from this fact that the primary factor for the spectral change is not in the disk technique itself but in the alkali halide used. By the application of the paste method, the effect of water adsorbed on alkali halides or other impurities can be made negligible since in this case the amounts of diacetamide and alkali halide are comparable to each other. Furthermore, the paste method is preferable to examine the corresponding spectral changes for diacetamide-*d* since the infrared spectra of highly pure diacetamide-*d* can be obtained only with a rapid technique such as the paste method. Considering these advantages of the paste method, we have carried out the measurements in the present study mainly on the

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1) For example, see O. Amakasu and A. Ito. *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 683 (1960). A number of literatures were cited in it.

2) V. C. Farmer, *Spectrochim. Acta*, **8**, 374 (1957).

3) A. W. Baker, *J. Phys. Chem.*, **61**, 453 (1957).

4) W. M. Padgett, II., J. M. Talbert and W. F. Hamner, *J. Chem. Phys.*, **26**, 959 (1957).

5) B. Cleverley and P. P. Williams, *Chem. & Ind.*, **1959**, 49.

6) T. Uno and K. Machida, This Bulletin, **34**, 545 (1961).

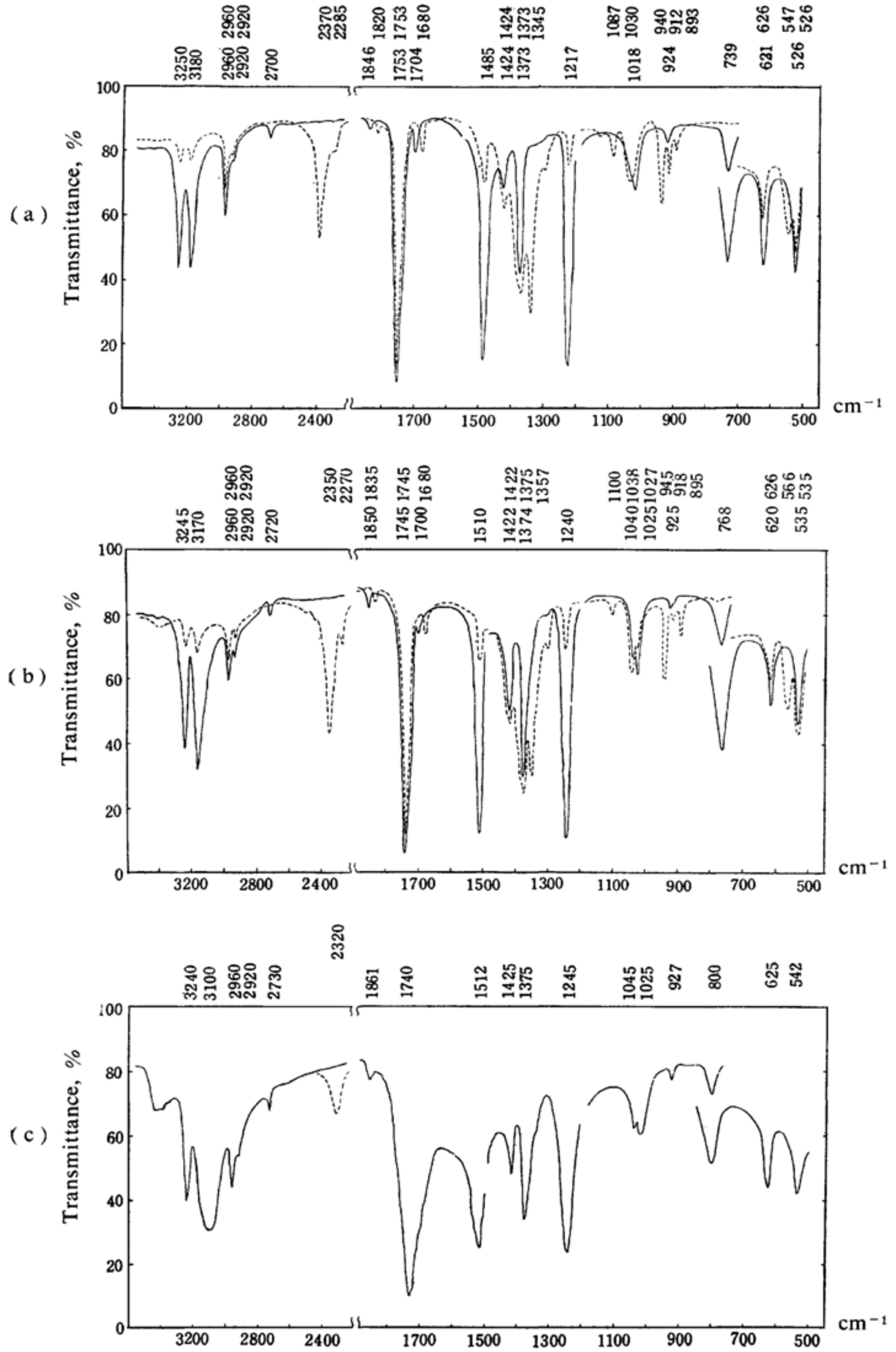

Fig. 1. Infrared spectra of diacetamide in the two-component systems containing alkali halides.

(a) Diacetamide-KI (3600～2200 cm^{-1} and 1550～1200 cm^{-1}, hexachlorobutadiene paste; 1900～1550 cm^{-1} and 1200～500 cm^{-1}, Nujol paste).

(b) Diacetamide-NaBr (3600～2200 cm^{-1} and 1490～1200 cm^{-1}, hexachlorobutadiene paste; 1900～1490 cm^{-1} and 1200～500 cm^{-1}, Nujol paste).

(c) Diacetamide-LiCl (3600～2200 cm^{-1} and 1490～1200 cm^{-1}, hexachlorobutadiene paste; 1900～1490 cm^{-1} and 1200～500 cm^{-1}, Nujol paste).

solid lines: undeuterated species.

broken lines: *N*-deuterated species.

pastes of the two-component systems of diacetamide and various alkali halides[7].

The infrared spectra of the two-component systems containing potassium iodide and sodium bromide are shown in Figs. 1, (a) and (b) respectively. It is obviously seen that these spectra resemble that of diacetamide in the form B[6]. These two-component systems show the sharp symmetric imide I band near 1750 cm^{-1} as well as the weak but well resolved antisymmetric imide I band near 1700 cm^{-1}. The latter band has been supposed to be overlapped by the broad symmetric imide I band in the spectrum of the undeuterated species in form B[8]. Furthermore, the low-frequency shift of the antisymmetric imide I band on deuteration is obviously observed for these two-component systems. There is only a little difference in the corresponding characteristic frequencies between the system containing sodium iodide and that containing potassium iodide. The system containing sodium bromide shows however, the infrared spectrum in which some characteristic frequencies related mainly to the N–H bond are appreciably different from those observed for the systems containing iodides. The similarity in the infrared spectra between form B and the two-component system containing one of these alkali halides is also observed in the case of diacetamide-*d*.

2) Potassium Bromide, Potassium Chloride and Sodium Chloride.—The infrared spectrum of the two-component system consist of form A and one of these alkali halides is identical with that of form A. In other words, these alkali halides bring about no spectral change. The comparison of alkali halides described in 1 and 2 suggests that both the cation and the anion of alkali halides participate in the spectral change under consideration.

3) Lithium Iodide, Lithium Bromide and Lithium Chloride.—These lithium salts bring about the spectral change. Infrared spectra analogous to Figs. 1, (a) and (b) are obtained for the systems containing lithium iodide and lithium bromide respectively. The infrared spectrum of the system containing lithium chloride is shown in Fig. 1, (c), which is appreciably different from either (a) or (b) in the regions 3600 to 2000 cm^{-1} and 1000 to 700 cm^{-1}. Since lithium halides adsorb an appreciable amount of water during the preparation of pastes, the examination of the spectral change for diacetamide-*d* on addition of lithium halides seriously suffers from the interference of the undeuterated species. Consequently, the characteristic bands of diacetamide-*d* in the two-component systems containing lithium halides could hardly be identified except for the N–D stretching band.

On the basis of the above fact, those infrared spectra obtained by the addition of these alkali halides may be conveniently classified into three types B_1, B_2 and B_3 according to the anion involved. Thus, we have three iodides, two bromides and one chloride giving rise to the spectral types B_1, B_2 and B_3 in that order. Differences among the types B_1, B_2 and B_3, as represented by Figs. 1, (a), (b) and (c) respectively, are mainly in the N–H (and N–D) stretching and the imide V (and V′) frequencies[6,8,9]. Table I shows these frequencies for each spectral type. The other characteristic frequencies[8] of diacetamide in the two-component systems are shown in Table II. Discussions on these frequencies will be given later.

TABLE I. THE CHARACTERISTIC FREQUENCIES (IN cm^{-1}) OF DIACETAMIDE DEPENDING ON THE ANION

Anion	I^-	Br^-	Cl^-	Form B[6]
Spectral types*1	B_1	B_2	B_3	
N–H Stretch.*2	3250m*3 3180m	3245m 3170 s	3240m 3100 s	3280 s 3205 s
Imide V	739m	768m	800m	739m
N–D Stretch.	2370m	2350m	2320m	2405 s
Imide V′	547m	566m	—	547m

*1 : See also Table III.

*2 : The origin of the splitting of this band was discussed in Ref. 9.

*3 : s, strong; m, medium.

TABLE II. THE CHARACTERISTIC FREQUENCIES (IN cm^{-1}) OF DIACETAMIDE DEPENDING ON BOTH THE ANION THE CATION

		Li^+	Na^+	K^+
Cl^-	Sym. imide I	1740 s		
	Imide II	1512 s		
	Imide III	1245 s		
	Imide II′	?		
	Imide III′	?		
Br^-	Sym. imide I	1740 s	1745 s	
	Imide II	1510 s	1510 s	
	Imide III	1245 s	1240 s	
	Imide II′	?	1357m	
	Imide III′	?	945m	
I^-	Sym. imide I	1742 s	1748 s	1753 s
	Imide II	1500 s	1490 s	1485 s
	Imide III	1237 s	1220 s	1217 s
	Imide II′	?	1349m	1345m
	Imide III′	?	941m	940m

Effect of Water. — Since lithium halides are extremely hygroscopic and it is difficult to

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[7] For the method of preparation of samples, see Experimental Part 2.

[8] T. Uno and K. Machida, This Bulletin, 34, 551 (1961).

[9] T. Uno and K. Machida, ibid., 34, 821 (1961).

avoid the adsorption of water during the preparation of pastes, the effect of a small amount of water on this spectral change must be taken into account if lithium halides are involved. Instead of removing water from the systems containing lithium halides, the other alkali halides were re-examined in the presence of a small amount of water⁽10⁾. The result was such that sodium chloride and potassium bromide partly give rise to the spectral change in the presence of water while potassium chloride does not.

These results are summarized in Table III, from which it is seen that the presence of water favors this spectral change. This may be understood in connection with the fact that the recrystallizing solvent for form B is water⁽6⁾. It is also seen however, that the ionic radii of the anion and the cation are concerned with this spectral change in both samples with and without water. In the alkali halide disk technique, the contamination of water is hardly avoidable since an excess of alkali halides which are usually hygroscopic must be used in comparison with the sample. As seen from Table III, the spectral change of diacetamide in the two-component system containing potassium bromide takes place only in the presence of water. Situations may be analogous for potassium bromide disks. The water adsorbed on the matrix partly gives rise to the spectral change related to the changes in intensities of the C=O stretching bands at 1734 and 1700 cm^{-1} previously mentioned.

TABLE III. THE SPECTRAL TYPES* OF DIACETAMIDE-ALKALI HALIDE SYSTEMS

		Li^+	Na^+	K^+
Cl^-	Without water	—	A	A
	With water	B_3	B_3 (partly)	A
Br^-	Without water	—	B_2	A
	With water	B_2	B_2	B_2 (partly)
I^-	Without water	—	B_1	B_1
	With water	B_1	B_1	B_1

* A is the identical spectrum with that of form A. B's are the spectra analogous to that of form B. Suffices differentiate the features of the N-H stretching and the imide V band (see text and Table I).

Effect of Compression in the Disk Technique.— When the disk technique is applied to form B of diacetamide with potassium bromide or potassium chloride as the matrix, it is observed that the absorption bands due to form A appear partly⁽11⁾. This fact may be interpreted in terms of the degradation of crystal lattices under pressure as has been reported for substances with melting points below 90°C⁽3⁾. Since diacetamide (m. p. 81°C) is crystallized in form A from the molten liquid⁽6⁾, it is not surprising that the degradation of form B is followed by the formation of form A. Thus, in the potassium bromide disk technique, the presence of water favors the change from form A to form B⁽12⁾ while the compression favors the reverse change. The infrared spectra of diacetamide in potassium bromide disks may vary with changes in these two factors.

Interaction between Diacetamide and Various Alkali Halides. — Differences in the characteristic frequencies among the two-component systems under consideration may be interpreted in terms of interaction between the -CONHCO- group and the ions of alkali halides. As seen from Table I, the N-H (and N-D) stretching and the imide V (and V′) frequencies depend only on the anion. This fact suggests the occurrence of an ion-dipole interaction between the imide hydrogen atom and the anion. Such an interaction, if any, is expected to become weaker as the ionic radius of the anion increases. The tendency of frequency shifts shown in Table I is in accord with this expectation. As the anion is changed from Cl^- through Br^- up to I^-, the N-H (and N-D) stretching frequency increases while the imide V (and V′) frequency decreases. On the other hand, as seen from Table II, the frequencies of the bands due mainly to the vibrations of the C=O or C-N bonds depend on both the cation and the anion, suggesting that there occurs another ion-dipole interaction between the C=O oxygen atoms and the cation of alkali halides. If otherwise, the frequencies shown in Table II should depend also only on the anion. Thus, the frequency differences shown in Tables I and II suggest that the ion-dipole interaction between the anion and the N-H bond and that between the cation and the C=O bonds occur simultaneously. Table II shows that the imide I frequency increases with the ionic radii of both the anion and the cation, while the imide II, III and II′ frequencies show the reverse shifts. The frequency shifts of the characteristic bands of monosubstituted amides depending on the polarity of the molecule have been well investigated⁽13⁾. Since similar shifts on the change of polarity are expected for the corresponding characteristic frequencies of acyclic imides, the above fact may be taken as indicating that the polar

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10) Estimation of the amount of water added was described in Experimental Part 3.

11) For the conditions of preparations of disks, see Experimental Part 4.

12) Strictly speaking, a certain form in which the -CONHCO- group takes a configuration similar to that in form B.

13) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 321, 619 (1956).

character of the molecule of diacetamide becomes more predominant as the ionic radii of the anion and the cation of alkali halide decrease. Furthermore, the symmetric imide I frequencies shown in Table II are higher than that of form B of diacetamide (1734 cm^{-1}). This fact means that the bond order of the C=O bond involved in the ion-dipole interaction with the cations is greater than that of the C=O bond involved in hydrogen bond in form B. The ion-dipole interaction between the cations and the C=O bonds seems to be so weak that this does not affect the nature of the N–H bond appreciably, resulting in the independence of the frequencies shown in Table I on the cation.

All the molecules of diacetamide in the two-component system under consideration can be involved in the ion-dipole interactions supposed from the spectral change only if the crystal lattice of form A degrades completely. This was confirmed by the powder X-ray diffraction measurement. Figure 2, (a) shows the diffraction pattern of the intimate mixture of diacetamide and potassium iodide (the molar ratio being approximately one to one)[14]. The diffraction pattern of diacetamide in form A is shown in Fig. 2, (b). It is seen that no diffraction line in (a) appears in (b). Thus, the crystal lattice of form A of diacetamide does not remain in the two-component system with potassium iodide. Furthermore, the appearance of new diffraction lines in (b) obviously indicates the formation of different lattices. These results give support to the explanation of the spectral change in terms of the ion-dipole interactions suggested above.

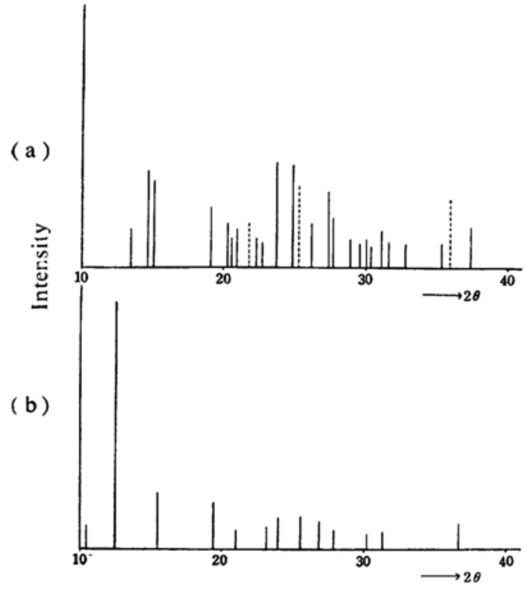

Fig. 2. Powder X-ray diffraction patterns.
(a) Diacetamide-KI system (Broken lines indicate the lines due to KI).
(b) Diacetamide in form A.

Table III shows that larger anions and smaller cations are favorable to give rise to the spectral change. Discussions will now be conducted regarding this fact on the basis of the ion-dipole interactions. The spectral change under consideration seems to be the evidence for the change in the configuration of the –CONHCO– group. Owing to the repulsive force between two oxygen atoms of the –CONHCO– group in the trans-trans configuration, the molecule in this configuration is expected to be less stable than that in the trans-cis configuration. In fact, as reported in the preceding paper[6], this is true for diacetamide. However, if a large anion such as I$^-$ approaches the hydrogen atom of a molecule in the trans-cis configuration, a strong repulsive force will be exerted between this anion and the oxygen atom at the cis position with respect to the hydrogen atom This repulsive force may be expected to increase with the ionic radius of the anion. On the other hand, if a cation approaches the oxygen atoms of a molecule in the trans-trans configuration, the repulsive force between these two oxygen atoms will be partly compensated for by the attractive forces between this cation and the oxygen atoms. The smaller the cation is, the more closely it can approach these oxygen atoms, so that the repulsive force between these two oxygen atoms decreases with the ionic radius of the cation. Thus, the simultaneous effects of the cation and the anion will give rise to the inversion from the trans-cis configuration to the trans-trans one and, as the experiment shows, the larger the anion and the smaller the cation of alkali halide are, the more easily the inversion takes place.

The actual situation in the crystalline state may be somewhat different from the monomolecular model for the ion-dipole interaction supposed above. However, it is noticed here that such a simplified model is sufficient for the qualitative elucidation of the marked spectral change. From the above discussions, it is expected that the energy difference between the trans-cis and the trans-trans configuration is rather small for diacetamide. Besides the electrostatic and the steric contribution to the energy, the energy of the formation of hydrogen bond must be taken into account to estimate the energy difference between these two configurations. However, as the problem is related to the solid state, it is difficult to determine which of these two configurations has the greater advantage for the formation of

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14) See Experimental Part 5.

hydrogen bond, whose natures may be very different from each other for these two configurations.

Conclusion

It has been found that the alkali halide disk technique gives rise to marked changes in infrared spectra of diacetamide under some conditions. This phenomenon has been proved to be related to the contamination of water, to the compression in this technique and to the ionic radii of the anion and the cation of alkali halide used. Similar spectral changes of diacetamide on the addition of various alkali halides have been interpreted in terms of the inversion of the -CONHCO- group from the trans-cis to the trans-trans configuration. In a qualitative consideration on the basis of both the electrostatic interactions and the steric effect, it has been pointed out that the possibility of the inversion is closely related to the ionic radii of both the cation and the anion.

Experimental

1) **Materials.** — Commercially available G. P. grade sodium chloride and potassium chloride were purified according to Hales' method[15]. Commercially available E. P. grade lithium iodide and lithium bromide, G. P. grade potassium iodine, potassium bromide, sodium iodide, sodium bromide and lithium chloride were used without further purification. These alkali halides were ground to 200 mesh, dried over phosphorus pentoxide at 150~200°C, in 5~10 mmHg for 10~15 hr., and stocked over phosphorus pentoxide in a vacuum desiccator. The preparation of form A and form B of diacetamide and diacetamide-*d* has been described[6].

2) **Preparation of Pastes.** — Each of the alkali halides (2~3 mg.) described in 1 was added on a drop of Nujol or hexachlorobutadiene in an agate mill and ground by hand carefully. Then form A of diacetamide or diacetamide-*d* (2~3 mg.) was added and ground by hand rapidly for ca 30 sec. The pastes thus obtained were immediately subjected to measurement. The preceding paper will be referred to for the details of the measurement[6].

3) **Effect of Water.** — Water was added with a thin glass rod on the sample containing each of potassium iodide, potassium bromide, potassium chloride, sodium iodide, sodium bromide and sodium chloride, and pastes were prepared as described in 2. The amounts of both water and diacetamide were adjusted so that the relative intensities of the O-H and the N-H stretching bands were similar to those of the corresponding bands observed for the samples containing lithium halides. In most cases the transmittance for the band maxima near 3400 and 3200 cm^{-1} were 60~70% and 30~50% respectively.

4) **Preparation of Disks.** — Potassium chloride or potassium bromide (ca. 500 mg.) and diacetamide in form B (1~2 mg.) were ground by hand in an agate mill for 3~5 min., and pressed under 120 kg./cm^2 in 2~3 mmHg for ca. 5 min. to prepare a disk.

5) **X-Ray Diffraction Measurement.** — Form A of diacetamide (ca. 500 mg.) and potassium iodide (ca. 830 mg.) were ground by hand carefully for 20~30 min., allowed to stand in a vacuum desiccator containing phosphorus pentoxide for a day, and subjected to the diffraction measurement (Fig. 2, (a)). Form A of diacetamide was treated similarly except for the addition of potassium iodide (Fig. 2, (b)). A Rigaku Denki X-ray diffractometer with GM counter was used and the Cu-K$_\alpha$ line was adopted.

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[15] J. L. Hales and W Kynaston, *Analyst*, 79, 702 (1954).