Infrared Spectroscopic Evidence for Two Forms of the Hydrogen-bonded Dimethylacetamide–Hydrogen Iodide Complex isolated in an Argon Matrix

Zofia Mielke[a] **and Austin J. Barnes**[b]

[a] *Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

[b] *Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.*

In argon matrices, infrared radiation dissociates the strongly hydrogen-bonded dimethylacetamide–hydrogen iodide complex to form a weakly hydrogen-bonded complex, which may be converted back into the strongly bonded form by raising the temperature of the matrix.

The hydrogen-bonded complexes formed between hydrogen halides and bases have been intensively studied in recent years using both experimental and theoretical techniques.[1] There are no gas-phase spectroscopic data for strongly hydrogen-bonded complexes in which the proton is shared between the base and halide or transferred to the base to form an ionic complex; a study of the complex isolated in an inert matrix such as argon provides the best available approach to the behaviour of the gas-phase complex. The most systematic studies using matrix isolation spectroscopy have been on the amine–hydrogen halide complexes, for which the extent of proton transfer was found to correlate with the normalised proton affinity difference between the amine and the halide ion.[2] Recent *ab initio* calculations[3] predict essentially the behaviour observed in argon matrices.

Recently we have studied the complexes formed between *N,N*-dimethylacetamide (DMA) and hydrogen halides.[4] It has been established[5] that the carbonyl oxygen is the predominant basic centre in DMA; its gas-phase proton affinity of 907 kJ mol^{-1} lies close to that of methylamine.[6] The spectra of the 1:1 DMA–hydrogen halide complexes in argon matrices are characteristic of strongly hydrogen-bonded complexes with the extent of proton transfer to the amide increasing from HCl to HBr to HI. For DMA–HI, the most prominent absorptions due to the complex are at 808 (broad) and 565 cm^{-1} and may be assigned to the $O \cdots H \cdots I$ antisymmetric stretching and bending modes respectively. Weaker bands due to the 1:1 complex were observed at 1374, 1277 (shoulder), and 1043 cm^{-1}. Other bands were identified as due to a DMA–$(HI)_2$ complex by comparison of spectra recorded over a range of relative concentrations of DMA and HI in argon matrices. An i.r.-induced process was found to occur, resulting in the disappearance of the bands assigned to the 1:1 complex and the appearance of a new sharp band at 1664 cm^{-1}, close to the C=O stretching absorption of monomer dimethylacetamide (1676 cm^{-1}). Very weak features also appeared at 1356 and 592 (shoulder) cm^{-1}, close to the $(C)CH_3$ symmetric deformation and C=O in-plane bending absorptions of the monomer (1352 and 587 cm^{-1} respectively). Warming the matrix to 30—35 K for a few minutes reversed the process, leading to essentially the original spectrum (Figure 1). These processes were found to be entirely reproducible. The kinetics of the i.r.-induced process were studied by measuring the rate of change of intensity of the 565 cm^{-1} band; it fitted approximately a first-order rate law with a half-life of *ca.* 2 h in the unfiltered beam of a Perkin-Elmer 180 spectrometer. The process was not affected by a filter which blocks all radiation above 4200 cm^{-1}, demonstrating that it is indeed caused by i.r. radiation. An InSb filter, which blocks all radiation above 1300 cm^{-1}, was found to prevent the change. Further filter studies are in progress to identify the range of wavelengths responsible for the photochemical process.

The only previous report of an i.r.-induced change in the spectrum of a complex trapped in a matrix is for dimethyl ether–hydrogen iodide in a nitrogen matrix.[7] The change was ascribed to transfer of the proton from a $[Me_2O \cdots H \cdots OMe_2]^+ I^-$ ion pair back to the anion. In the present example, the i.r.-induced process could either form the ionic complex $DMAH^+ I^-$ or dissociate the strongly hydrogen-bonded $DMA \cdots H \cdots I$ complex to give a weakly interacting $DMA \cdots HI$ pair. Either way, the product is clearly less stable than the original strongly hydrogen-bonded complex since it is converted back on warming the matrix. Similar processes have been observed in the rotamerisation of some small molecules in matrices.[8] By analogy with these conformational changes,

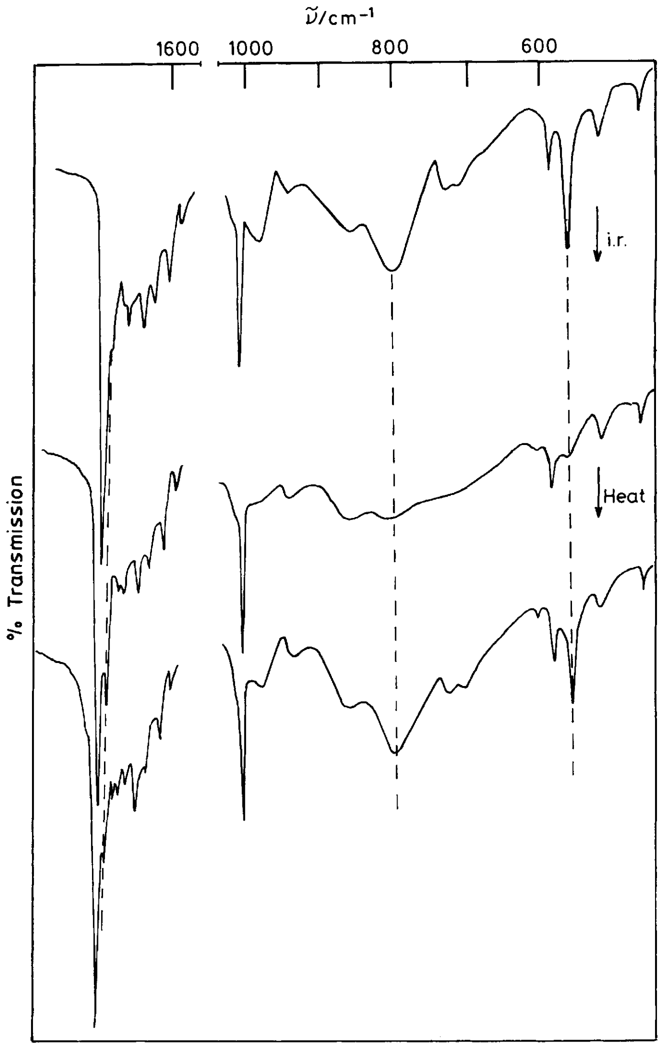

Figure 1. I.r. spectra of a mixture of DMA:Ar (1:600) + HI:Ar (1:300) at *ca.* 20 K recorded immediately after deposition (top), after 6 h irradiation in the beam of the i.r. spectrometer (middle), and after annealing at 30—35 K for a few minutes (bottom).

the necessity to warm the matrix to 30—35 K in order to reconvert the product into the original complex implies an activation energy of *ca.* 7 kJ mol^{-1} for this process. The InSb filter study shows that *at least* 15.5 kJ mol^{-1} (1300 cm^{-1}) are required for the i.r.-induced process. Thus the strongly hydrogen-bonded complex corresponds to a much deeper potential minimum than the product of the photochemical process.

Determination of which of the possible i.r.-induced processes is occurring depends on the identification of the band at 1664 cm^{-1}. The i.r. spectrum of the iodide salt of DMA exhibits strong bands at 2720 (OH stretch, v br.), 1685 (C=N stretch), and 1391 cm^{-1} (C–O stretch).[9] The 1664 cm^{-1} band could be the C=N stretch of the salt isolated in an argon matrix, with the OH stretch too broad to be detected and the C–O stretch obscured by the strong DMA absorptions around 1400 cm^{-1}. The C=N stretching absorption in the solid phase is comparatively broad (half-height band width *ca.* 20 cm^{-1}) but may become appreciably sharper in the matrix. A more reasonable explanation is that the 1664, 1356, and 592 cm^{-1} bands are due to the perturbed vibrations of a DMA molecule interacting weakly with a hydrogen iodide molecule. The perturbed C=O stretching mode at 1664 cm^{-1} implies that the HI is weakly hydrogen-bonded to the carbonyl group of the DMA molecule.

The authors are grateful to Professor H. Ratajczak for helpful discussions and to Dr M. A. Ford of Perkin-Elmer Ltd. for the loan of filters.

Received, 2nd April 1985; Com. 445

References

1 A. J. Barnes, *J. Mol. Struct.*, 1983, **100**, 259.
2 B. S. Ault, E. Steinback, and G. C. Pimentel, *J. Phys. Chem.*, 1975, **79**, 615; L. Schriver, A. Schriver, and J. P. Perchard, *J. Am. Chem. Soc.*, 1983, **105**, 3843; A. J. Barnes, T. R. Beech, and Z. Mielke, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 455; A. J. Barnes, J. N. S. Kuzniarski, and Z. Mielke, *ibid.*, 1984, **80**, 465; A. J. Barnes and M. P. Wright, *ibid.*, submitted for publication.
3 A. Brciz, A. Karpfen, H. Lischka, and P. Schuster, *Chem. Phys.*, 1984, **89**, 337; Z. Latajka, S. Sakai, K. Morokuma, and H. Ratajczak, *Chem. Phys. Lett.*, 1984, **110**, 464.
4 Z. Mielke and A. J. Barnes, to be published.
5 P. Stilbs, S. Forsen, and J. S. Hartman, *J. Chem. Soc., Perkin Trans. 2*, 1977, 556; C. de Loze, P. Combelas, P. Bacelon, and C. Garrigou-Lagrange, *J. Chim. Phys. Physicochim. Biol.*, 1972, **69**, 397; L. Bernander and G. Olofsson, *Tetrahedron*, 1972, **28**, 3251.
6 S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.
7 L. Schriver, A. Loutellier, and A. Burneau, *Chem. Phys. Lett.*, 1979, **60**, 471.
8 A. J. Barnes, *J. Mol. Struct.*, 1984, **113**, 161.
9 D. Cook, *Can. J. Chem.*, 1964, **42**, 2721.