Tetrahedron Vol. 37, No. 18, pp. 3107 to 3110, 1981
Printed in Great Britain.

0040-4020/81/183107-04$02.00/0

THE MECHANISM OF [1,3] O TO N ACYL MIGRATIONS
A MNDO SCF-MO STUDY

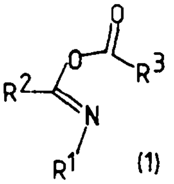
Henry S. Rzepa

(Received in UK 2 July 1981)

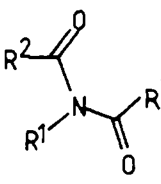
Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY.

Abstract MNDO SCF-MO calculations suggest that the uncatalysed rearrangements of O-acyl imidates (1) to the corresponding imides (2) are concerted reactions involving synchronous C-N bond formation and C-O bond cleavage. The calculated dipole moment and atomic charges in the transition state are consistent with the properties of these reactions in solution. The transition states for [1,3] acyl migrations in compounds such as 3 which have no lone pair of electrons are predicted to have significantly different properties.

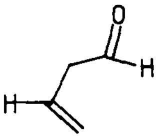
Although rearrangements of the type 1 to 2 have been extensively studied in solution,[1,2] the mechanism of the uncatalysed reaction remains uncertain. Both a stepwise process involving either a tetrahedral intermediate or a caged radical pair, and a concerted reaction *via* either a [1,3] sigmatropic acyl shift or nucleophilic substitution on the carbonyl group are possible.



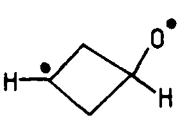
(1)



(2)



(3)



(5)

In order to distinquish between these alternatives, the potential energy surfaces for these reactions have been investigated using the MNDO semi-empirical SCF-MO procedure.[3] This method, whilst computationally much faster than *ab initio* methods,[4] has been shown to predict the heats of formation of a wide variety of compounds with reasonable accuracy,[3] and to predict transition state structures for *e.g.* the loss of hydrogen halide from haloalkanes, which are similar to those obtained using *ab initio* theory.[5]

COMPUTATIONAL PROCEDURE

The unsubstituted compounds (1, R^2=R^3=H, R^1=H,OH; 2, R^2=R^3=H, R^1=H,OH) were selected as models for the reaction and their energies and geometries were calculated using the standard spin-restricted (RHF) MNDO method.[3] All geometrical variables were optimised with respect to the calculated energy using the Davidon-Fletcher-Powell algorithm.[3] The potential-energy surfaces for the interconversion of 1 and 2 were obtained by evaluating the energy at several fixed values of both the C-O and the C-N bond lengths, all other geometrical variables being optimised. Location of the saddle points in the potential-energy surfaces (*e.g.* Figures 1 and 2) gave estimates of the transition state structures, which were further refined by minimising the squares of the derivatives of the energy with respect to each geometrical variable[6]. The resultant stationary points were characterised by calculating the corresponding force-constant matrix[7]. These matrices each had only one negative eigenvalue and an associated eigenvector which corresponded to the correct reaction coordinate (Figures 1 and 2).

RESULTS AND DISCUSSION

The most stable conformations for 1 and 2 involved a weak interaction between the lone pair of electrons on the nitrogen or oxygen atom and the acyl carbon atom (Figures 1 and 2). The imide (2, R^1=H) was calculated to be 16.1 kcal/mol more stable than the isomeric imidate (1, R^1=H), whereas for R^1=OH, 1 and 2 were calculated to be closer in energy.

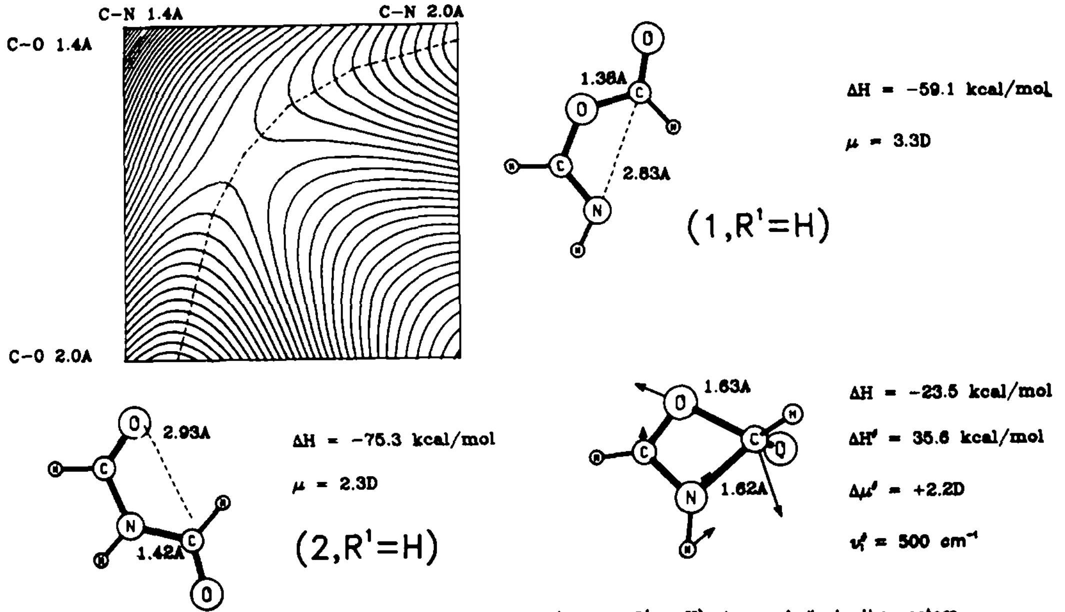


Figure 1. Potential energy surface for the rearrangement of (1 → 2, R^1 = H). Arrows indicate the vectors corresponding to the calculated reaction coordinate.

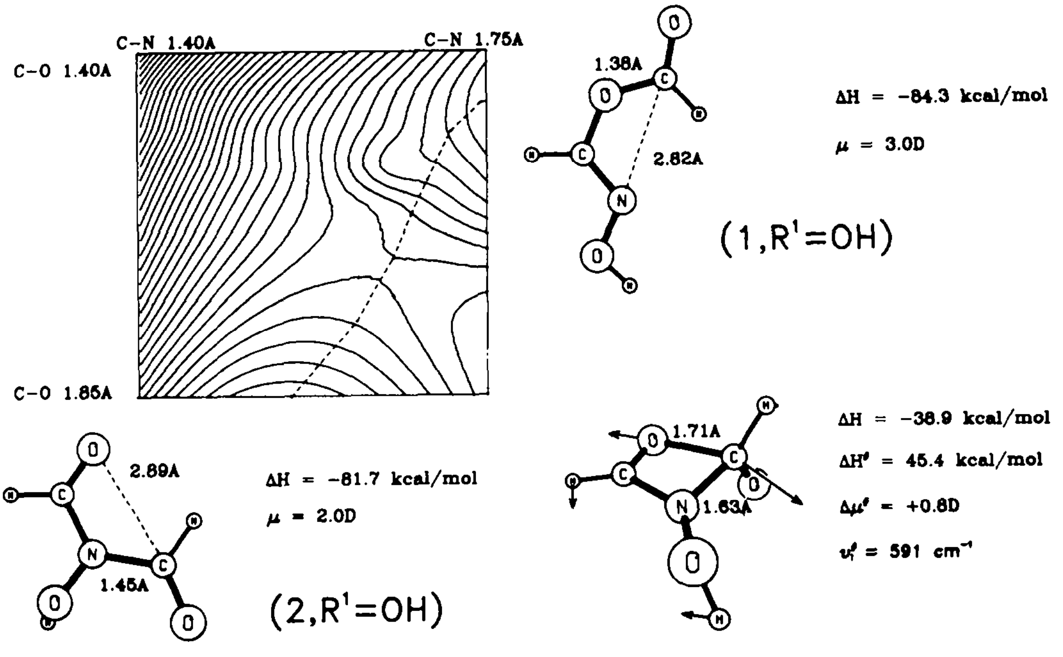


Figure 2. Potential energy surface for the rearrangement of (1 → 2, R' = OH).

These results are supported by the evidence available for similar compounds.[2,8] The nature of the potential energy surfaces (Figures 1 and 2) suggests that the rearrangements are concerted and not stepwise, involving essentially synchronous attack by the nitrogen lone pair on the carbonyl group and cleavage of the C-O bond. The four-centred cyclic transition states are planar with tetrahedral coordination of the acyl carbon atom. This role of the lone pair is fully consistent with the observation[1] that only the E and not the Z geometrical isomers rearrange. The calculated activation energy for R^1=OH (45.4 kcal/mol) is about 20 kcal/mol higher than observed for the rearrangement of aryl substituted species in solution.[1] This may be due to the simplicity of the model used in these calculations, in which solvent effects and the role of stabilising substituents (e.g. R^2=R^3=ArX) are neglected, and to the tendency[5] of the **MNDO** method to overestimate enthalpies of activation by up to 30%. The barrier to the rearrangement of the O-acyl imidate (1,R^1=H) is predicted to be 9.8 kcal/mol lower than that of the hydroximic anhydride (1,R^1=OH), which is supported by the observed relative instability of O-acyl imidates and their very rapid rearrangement to imides.[1,2]

The calculated dipole moment of the transition state for the rearrangement of (1,R^1=OH) is only 0.8D greater than that of the reactant itself, which is consistent with the report[1] that the rates of these reactions show a low sensitivity to the polarity of the solvent. It has also been observed that electron withdrawing substituents can either decrease (R^1=OCH_2ArX, R^2=ArX) or increase (R^3=ArX) the rate of rearrangement.[1] The calculated atomic electron densities show a build up of positive charge in the transition state at the oxygen atom of R^1=OH (by +0.05e), and at the carbon atom bearing R^2 (by +0.14e), which is consistent with the observed substituent effects at these positions. The acyl carbon atom is also calculated to become more positive (by 0.10e), although the change in hybridisation and co-ordination at this centre makes the interpretation of the atomic charges in terms of substituent effects less easy.

The transition state for the degenerate rearrangement of 3, which has no corresponding lone pair, has quite different properties. It was initially located by enforcing a plane of symmetry and using the standard single configuration **RHF-MNDO** procedure. The optimised geometry (e.g. 4, Figure 3) is significantly non-planar, corresponding closely to a [1,3] suprafacial sigmatropic shift with "inversion of configuration" at the acyl carbon atom.

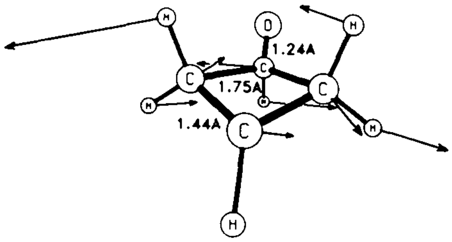


Figure 3 Transition state for the [1,3] Acyl migration in (3) calculated using the single configuration spin restricted method

The calculated enthalpy of activation (86.5 kcal/mol) is very much higher than the corresponding value (e.g. 45.4 kcal/mol) for the reaction of (1, R^1 = OH), which suggests that this structure may have significant biradical character. Re-optimisation of the geometry using a spin-unrestricted version of **MNDO** (**UMNDO**),[9] which has been shown to give reasonable estimates of the geometries of biradical-like species,[10] resulted in a structure which was planar and significantly different from that of 4. The wavefunction corresponded to the biradical 5 and inspection of the calculated force-constant matrix showed it to be an energy minimum. Since use of the **UMNDO** method leads to unreliable estimates of the energy,[11] the biradical 5 was also studied using a spin-restricted version of **MNDO** which includes configuration interaction (CI) involving single and double excitations from the HOMO to the LUMO. This method predicted a geometry for 5 (Figure 4) which was virtually identical to that given by the **UMNDO** method[12] and an energy which was 29 kcal/mol lower than that found previously for 4 using the single configuration **RHF-MNDO** procedure (Table). This difference is sufficiently large to suggest that the rearrangement of 3 might proceed *via* a biradical intermediate, and is a stepwise and not a concerted reaction.

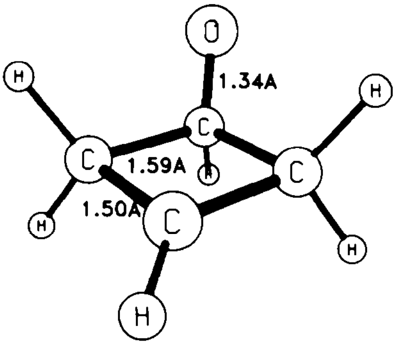


Figure 4. Calculated structure of (5) using the Spin-Restricted/3x3 CI procedure.

Significantly, when the molecular geometry is **not** re-optimised, the calculated energy of 4 is little affected by inclusion of such a **CI** (Table), demonstrating how essential such re-optimisation is if misleading results are to be avoided. Both the **UMNDO** and the **CI** methods predict geometries and energies for 1 and the transition states for the rearrangements to 2 which are essentially identical to those obtained using the single configuration **RHF-MNDO** method. This suggests that these particular reactions have little biradical character and are truly concerted.

TABLE. Calculated MNDO Energies for 3 - 5

	3	4	5
ΔH_f^{a}	-20.7	65.8	84.2^{d}
ΔH_f^{b}	-20.7	56.7^{d}	25.2
ΔH_f^{c}	-17.3^{d}	71.3^{d}	37.3

[a] Single configuration **RHF** method, kcal/mol. [b] UMNDO method. [c] **RHF/3x3 CI** method. [d] No geometry re-optimisation.

Acknowledgements. The Science Research Council are thanked for their award of an Advanced Postdoctoral Fellowship. The calculations were carried out on the CDC 7600 computer at the University of London Computer Centre. The figures were generated at Imperial College Computer Centre using the interactive graphical facilities and the text was set using the word processing program MTROFF.

References and Notes.

[1] D. G. McCarthy and A. F. Hegarty, J. Chem. Soc. Perkin 2, 1977, 1085.

[2] C. G. McCarty in "The Chemistry of the Carbon-Nitrogen Double Bond", ed. S. Patai, Wiley-Interscience, New York, 1970, ch. 9; C. G. McCarty and L. A. Garner in "The Chemistry of Amidines and Imidates", ed. S. Patai, Wiley-Interscience, New York, 1975, ch. 4.

[3] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 1977, **99**, 4899, 4903; M. J. S. Dewar and M. L. McKee, ibid, 1977, **99**, 5841; M. J. Dewar and H. S. Rzepa, ibid, 1978, **100**, 78, 770; M. J. S. Dewar, M. L. McKee and H. S. Rzepa, ibid, 1978, **100**, 3800.

[4] M. J. S. Dewar and G. P. Ford, J. Am. Chem. Soc.,, 1979, **101**, 5558.

[5] H. S. Rzepa, J. Chem. Soc., Chem. Commun., submitted for publication.

[6] P. K. Weiner, Ph. D. Dissertation, Austin, Texas, 1974.

[7] M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa, W. Thiel and Y. Yamaguchi, J. Mol. Struct., 1978, **43**, 135.

[8] D. G. McCarthy and A. F. Hegarty, J. Chem. Soc. Perkin 2, 1977, 1080.

[9] M. J. S. Dewar, S. Olivella and H. S. Rzepa, Chem. Phys. Lett., 1977, **47**, 80.

[10] This method is computationally very much faster than **RHF CI** procedures and leads to very similar optimised geometries. Calculation of the force constant matrix is also significantly faster.

[11] M. J. S. Dewar, S. Olivella and H. S. Rzepa, J. Am. Chem. Soc., 1978, **100**, 5650.

[12] The **UMNDO** geometry was used as a starting point for the optimisation. A general problem with the calculation of geometries using **CI** methods is that there is no certainty that the configurations selected will be equally important at the initial geometry and at the final optimised geometry unless these are fairly similar, or unless a large number of configurations are included in the **CI**.