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Original investigations

A qualitative determination of the favourable nuclear pathway for the ground state decomposition of formyl-fluoride

V. Bachler[1], E. A. Halevi[2] and O. E. Polansky[1]

[1] Max-Planck-Institut für Strahlenchemie, Stiftstr. 34–36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany
[2] Technion-Israel Institute of Technology, Department of Chemistry, Technion City, Haifa 32000, Israel

A qualitative, symmetry-independent, procedure is applied to the thermal decomposition of formyl-fluoride in order to single out energetically favourable directions on the potential energy surface for its fragmentation to carbon monoxide and hydrogen fluoride. The qualitative results are in good agreement with published calculations for the favoured decomposition pathway and compatible with experimental results.

Key words: Potential energy surface—MO-correlation diagrams

1. Introduction

Correlation diagrams based on the symmetry properties of molecular orbitals are valuable aids in the determination of energetically favourable reaction pathways. A correlation diagram technique which employs symmetry efficiently is Orbital Correspondence Analysis in Maximum Symmetry (OCAMS) [1, 2]. A correlation diagram is constructed for a nuclear pathway possessing the highest common symmetry of reactant *R* and product *P*. Then, if not all of the occupied orbitals of *R* correlate with those of *P*, and the high-symmetry pathway is "forbidden" as a result, OCAMS provides rules for choosing those nuclear displacements which point towards a reaction path which is "orbital-symmetry allowed" in lower symmetry and energetically favourable.

OCAMS has been successfully applied to the various photochemical decomposition modes of formaldehyde [3]. It was shown that the reaction $H_2CO \rightarrow H_2 + CO$, which is believed to take place on the electronic ground-state potential energy surface [4], proceeds along a planar but asymmetric reaction path. This conclusion is in full agreement with accurate computational results [5, 6], but it would have had only limited utility as an *a priori* guide to such calculations. This is because it merely predicts the reaction path to be a linear combination, with unknown coefficients, of the five in-plane symmetry coordinates of CH_2O, excluding only the out-of-plane bending coordinate.

A situation similar to that just described will occur whenever the overall symmetry is so low that all of the internal coordinates are distributed among a very few irreducible representations. In such cases, the need arises for a criterion which goes beyond qualitative considerations of symmetry and is able to select the energetically most favourable pathway from among several which are symmetry-allowed. Arguments based on symmetry alone are, of course, completely inadequate in the extreme case of a reaction which is "allowed" along any totally symmetric pathway, because all of the occupied orbitals of R and P intercorrelate in the point group of highest common symmetry. In order to fill this need, a procedure has recently been proposed which, although it too is based on the correlation of molecular orbitals, does not depend explicitly on their symmetry properties [7].

Consider two different nuclear arrangements $\boldsymbol{R}$ and $\boldsymbol{P}$ located on a ground state potential energy surface. We are interested in the energetic requirements for proceeding from $\boldsymbol{R}$ to $\boldsymbol{P}$ along some preselected pathway. This pathway may be thought of as a sequence of intermediate nuclear geometries $\boldsymbol{I}$, at each of which the approximate energy $E(\boldsymbol{I})$ is given by [7]

$$E(\boldsymbol{I}) = \underset{(a)}{[E(\boldsymbol{R}) + \langle R|V(\boldsymbol{I})|R\rangle]} + \underset{(b)}{\frac{[\langle R|V(\boldsymbol{I})P\rangle - \langle R|P\rangle(E(\boldsymbol{I}) - E(\boldsymbol{R}))]^2}{E(\boldsymbol{I}) - \langle P|H(\boldsymbol{I})|P\rangle}}. \tag{1}$$

$E(\boldsymbol{R})$ designates the electronic energy of the nuclear arrangement $\boldsymbol{R}$; $H(\boldsymbol{I})$ is the Hamiltonian operator for the electronic energy when the nuclei are fixed at the geometry $\boldsymbol{I}$; $V(\boldsymbol{I})$ is a one-electron operator for the difference in the nuclear–electron interaction which arises when the geometry $\boldsymbol{R}$ is transformed into $\boldsymbol{I}$. The wavefunctions $|R\rangle$ and $|P\rangle$ represent Hartree–Fock one-determinantal wavefunctions, which contain the occupied orbitals $\{r_i\}$ and $\{p_i\}$, respectively, calculated at the different geometries $\boldsymbol{R}$ and $\boldsymbol{P}$. The analysis performed in [7] shows that the term (b) in Eq. (1) is always negative. Therefore, a pathway from $\boldsymbol{R}$ to $\boldsymbol{P}$ is assumed to be of low energy provided the magnitude of this term is appreciable, as will be the case when all occupied orbitals r_i and p_i overlap significantly pairwise. If this situation holds for all orbitals except for one pair, r_m and p_m, which have a smaller overlap integral, contribution (b) will be small, and a nuclear displacement from $\boldsymbol{R}$ to $\boldsymbol{P}$ should be energetically unfavourable [7]. In that case, however, the form of the overlap function $\rho_{mm} = r_m p_m$ can be exploited in order to find favourable deviations from the high energy pathway [7].

In the present communication we utilize this procedure for singling out energetically favourable directions on the potential energy surface for the decomposition of formyl fluoride (OCHF), and compare the results with available calculations of the decomposition pathway [8, 9]. We first select a trial reaction path, such as might be suggested by intuition, and show that although it is symmetry-allowed, it must be classified as energetically unfavourable. Afterwards, we illustrate how to deviate from this pathway in directions on the potential energy surface that are energetically more favourable.

2. A symmetry allowed but energetically unfavourable pathway

An easily visualized trial pathway for the decomposition of OCHF into carbon monoxide (CO) and hydrogen fluoride (HF) is schematically depicted in Fig. 1. The first point on the adopted pathway ($\boldsymbol{R}_0$) is a modified geometry of OCHF in which the CH and CF bond lengths are equal and the angles ∡OCH and ∡OCF are assigned the same values. These deviations from the equilibrium geometry of OCHF do not effect the energetic ordering of the molecular orbitals and are unimportant for the qualitative analysis which follows. The decomposition is simulated by an increase of the distance $R_{\mathrm{C-M}}$ between the C-atom and the midpoint M of the H—F distance by increments of 0.5 a.u., the H—F distance being concurrently decreased in steps of 0.2 a.u. (see Fig. 1). At $R_{\mathrm{C-M}} = 4$ a.u.,

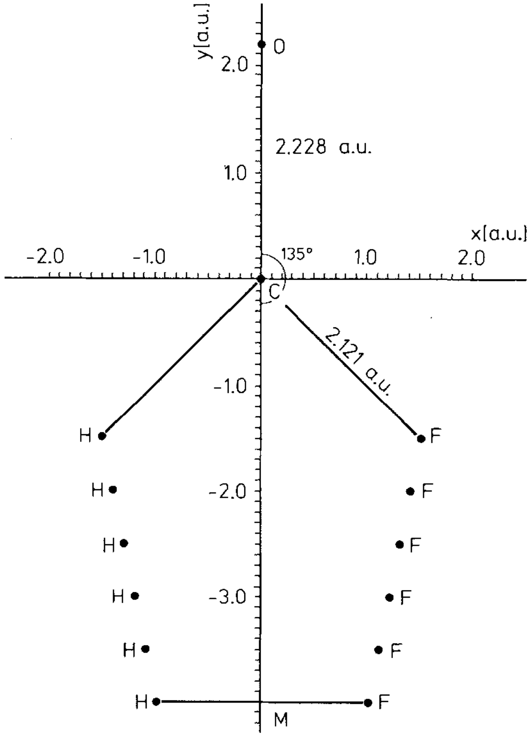

Fig. 1. Arbitrarily adopted nuclear pathway for the decomposition of OCHF into CO and HF. The x and y axes are scaled in atomic units

the interaction between the separating fragments is sufficiently so small that the corresponding geometry may be taken as $\boldsymbol{P}_0$.

The molecular orbitals at the successive geometries of the adopted pathway were calculated *ab initio* using the STO-3G basis set [10]. The energies of the three highest occupied and the three lowest unoccupied orbitals are represented in Fig. 2 by filled circles. Both formyl fluoride in geometry $\boldsymbol{R}_0$ and its separated fragmentation products, oriented in geometry $\boldsymbol{P}_0$, have the same electronic configuration in C_s: $[10\times a'^2, 2\times a''^2]$. Therefore, our trial pathway for thermal decomposition of OCHF to CO and HF is formally allowed by orbital symmetry. The question that obtrudes itself is whether this is a sufficient condition for characterizing it as a lowest energy reaction path.

In order to address this question, we convert Fig. 2 into an orbital correlation diagram, connecting the successive points by correlation lines. However, instead

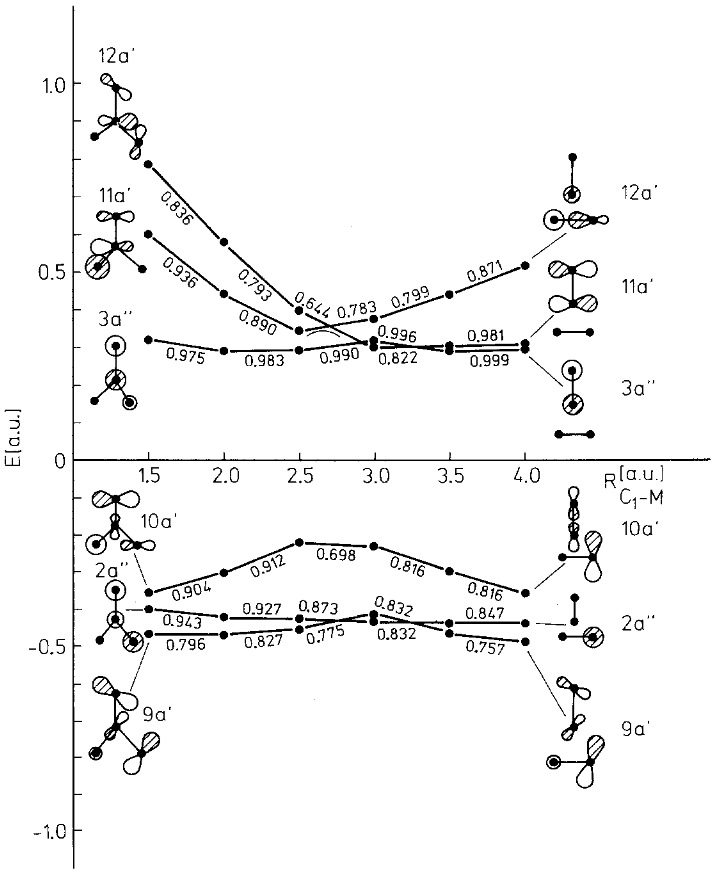

Fig. 2. Correlation diagram for the molecular orbitals along the decomposition pathway of Fig. 1. The calculated MO energies are represented by filled circles; the numbers in the diagram are the absolute values of the overlap integrals between orbitals connected by the correlation line

of applying the non-crossing rule in the low C_s symmetry of the adopted pathway, we employ an alternative procedure, proposed by R. D. Kelsey [11], which is independent of symmetry arguments: Consider two different, but adjacent nuclear configurations $\boldsymbol{R}$ and $\boldsymbol{P}$ on the pathway adopted. We derive two sets of molecular orbitals $\{r_i\}$ and $\{p_j\}$, comprising the electronic wave functions $|R\rangle$ and $|P\rangle$ respectively, and calculate the overlap integrals S_{ij}, where i runs over the six molecular orbitals of $|R\rangle$ that are shown in Fig. 2 and j runs over those of $|P\rangle$.

The numerical values of S_{ij}, are calculated with the $\{r_i\}$ and $\{p_j\}$ evaluated at $\boldsymbol{R}$ and $\boldsymbol{P}$ respectively, where all pairs of adjacent geometries $\boldsymbol{R}$ and $\boldsymbol{P}$ along the pathway from $\boldsymbol{R}_0$ to $\boldsymbol{P}_0$ have been considered. In agreement with what had been previously postulated, for a definite i, only one overlap integral $\langle r_i|p_k\rangle$ is large, whereas all others are considerably smaller [7]. Consequently, orbitals r_i and p_k are said to correlate because p_k is the orbital whose form most resembles the form of r_i, their similarity being manifested in a large overlap integral $\langle r_i|p_k\rangle$ [7]. The correlation lines drawn in Fig. 2 are those suggested by the largest overlap integrals; the absolute values of the overlap integrals are recorded at the appropriate segments.

Fig. 2 confirms that the ground state pathway of Fig. 1 is allowed, since the occupied orbitals of OCHF correlate with occupied orbitals of CO and HF. Additional information can be extracted from the MO-correlation diagram by considering all of the relevant overlap integrals $\langle r_i|p_j\rangle$ with molecular orbitals obtained at the intermediate geometries $\boldsymbol{R}$, in which $R_{C-M} = 2.5$ a.u. and $\boldsymbol{P}$, in which it is 3.0 a.u.; their absolute values are recorded in Table 1. The HOMO ($10a'$) of $\boldsymbol{R}$ is transformed into the HOMO ($10a'$) of $\boldsymbol{P}$, as indicated by a value of 0.698. However, the overlap integral between $10a'$ of $\boldsymbol{R}$ and $11a'$ of $\boldsymbol{P}$ has the comparable value of 0.586, whereas $10a'$ of $\boldsymbol{P}$ overlaps significantly with both $11a'$ (0.332) and $12a'$ (0.342) of $\boldsymbol{R}$. If the magnitude of the overlap integrals between molecular orbitals is considered as a measure for their similarity and the similarity is assumed to be large between correlating orbitals, the calculated values suggest an intended correlation [12] between occupied and unoccupied orbitals. Such an intended correlation implies an intended crossing of the $10a'$ and $12a'$ orbitals of OCHF along the trial pathway adopted.

This intended crossing permits a comparison with the correlation diagram in C_{2v} for the analogous fragmentation of formaldehyde to H_2 and CO (Fig. 1 of Reference 3). Orbital 10a′ of $\boldsymbol{R}$ is related to the highest occupied $2b_2$ orbital of CH_2O, whereas $10a'$ of $\boldsymbol{P}$ incorporates the $6a_1$ MO, which is predominantly the σ-orbital of CO. The elimination of H_2 from formaldehyde is forbidden at the MO level by the presence of a genuine crossing between the $2b_2$ and the $6a_1$ orbital, but the "forbiddenness" is relaxed by an in-plane distortion of species b_2, that reduces the symmetry of the nuclear frame to C_s, in which both b_2 and a_1 map onto a' [3]. The inherent substitutional asymmetry of formyl fluoride, which belongs to C_s ensures that the HOMOs of $\boldsymbol{R}$ and $\boldsymbol{P}$ both belong to the same totally symmetric representation. However, the intended crossing which makes the pathway unfavourable is still evident, suggesting that an in-plane deviation from the trial pathway might be energetically advantageous here too.

Table 1. Absolute values of the overlap integrals between the molecular orbitals for geometries ***R*** and ***P*** with $\boldsymbol{R}_{\mathrm{C-M}} = 2.5$ and 3.0 a.u. respectively. Dashed lines represent zero values which are due to the different symmetries of the orbitals

R \ P	HOMO−2 $(2a'')$	HOMO−1 $(9a')$	HOMO $(10a')$	LUMO $(11a')$	LUMO+1 $(3a'')$	LUMO+2 $(12a')$
LUMO+2 $(12a')$	—	0.013	0.342	0.644	—	0.458
LUMO+1 $(11a')$	—	0.261	0.332	0.212	—	0.783
LUMO (3a″)	0.017	—	—	—	0.990	—
HOMO $(10a')$	—	0.115	0.698	0.587	—	0.067
HOMO−1 (2a″)	0.873	—	—	—	0.030	—
HOMO−2 (9a′)	—	0.775	0.167	0.060	—	0.186

The unfavourableness of the trial pathway is also substantiated by the overlap integrals $\langle r_{10a'}|p_{10a'}\rangle$ between the HOMOs of geometries ***R*** and ***P*** along the correlation diagram depicted in Fig. 2. At the reactant and product sides of the diagram, near the geometries $\boldsymbol{R}_0$ and $\boldsymbol{P}_0$, respectively, values of ~ 0.9 are calculated (see Fig. 2). However, when ***R*** and ***P*** are assigned the intermediate $R_{\mathrm{C-M}}$ values of 2.5 a.u. and 3.0 a.u. respectively, the overlap integral decreases significantly to 0.698. It follows from the recently performed analysis [7], that the adopted trial pathway of Fig. 1 is energetically unfavourable, because it connects two adjacent geometries ***R*** and ***P*** between which the energy-lowering contribution (b) in Eq. (1) is characteristically reduced as a result of the decreased magnitude of the overlap integral.

3. The most favourable deviation from an unfavourable pathway

Having reached the conclusion that the initially adopted trial pathway is energetically unfavourable, we are in a position to determine directions leading away from it towards a more favourable decomposition pathway. For this purpose we exploit the form of the overlap function $\rho_{m,m} = r_m p_m$ between two orbitals r_m and p_m calculated at two adjacent nuclear configurations ***R*** and ***P***. The subscript m refers to a pair of occupied orbitals possessing a small overlap integral, which can therefore be assumed to be primarily responsible for the energy-barrier which makes the trial pathway unfavourable [7]. Here, we again use the geometries ***R*** and ***P*** with $R_{\mathrm{C-M}} = 2.5$ and 3.0 a.u. respectively (see Fig. 2), and consider $\rho_{\mathrm{HOMO,HOMO}}$, i.e. the overlap function between the orbitals $r_{10a'}$ and $p_{10a'}$, the overlap integral between which is 0.698.

Fig. 3 is a contour plot of $\rho_{\mathrm{HOMO,HOMO}}$ in the yx-plane, to which the pathway depicted in Fig. 1 is restricted. Dashed (continuous) lines connect points having

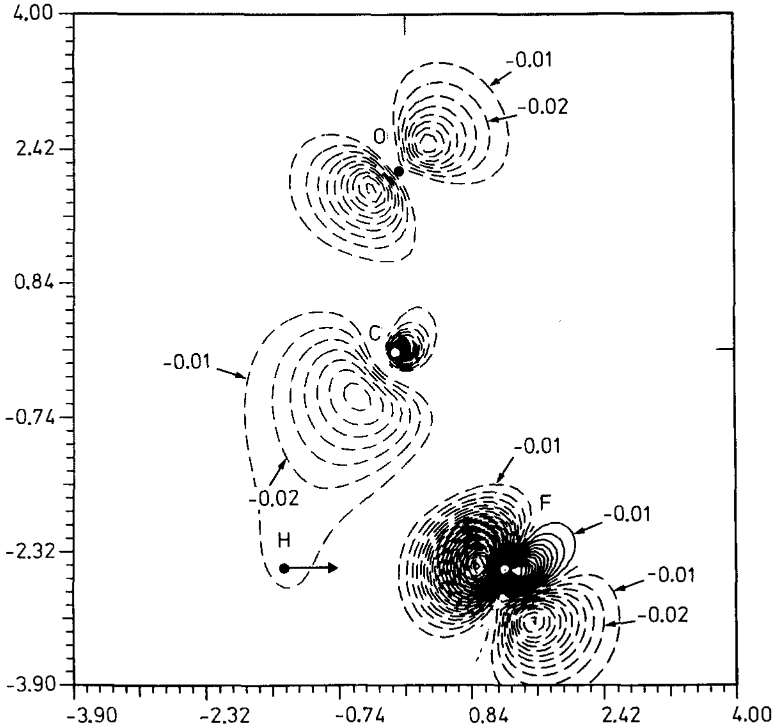

Fig. 3. Contour plot of the overlap function $\rho_{\mathrm{HOMO,HOMO}}$ between the orbitals r_{HOMO} of R with $R_{\mathrm{C-M}} = 2.5$ a.u. and the orbital p_{HOMO} of P with $R_{\mathrm{C-M}} = 3.0$ a.u. The plot represents negative (dashed line) and positive (continuous line) functional values of $\rho_{\mathrm{HOMO,HOMO}}$ in the plane of the pathway depicted in Fig. 1; the spacing of lines is 0.01

the same negative (positive) functional values. In addition, the positions of the nuclei in geometry $\boldsymbol{R}$ are also specified. Inspection of Fig. 3 shows that the C-atom is located in a region where $\rho_{\mathrm{HOMO,HOMO}}$ has a large negative value, whereas the O, H and F atoms are situated in positions where the functional values of $\rho_{\mathrm{HOMO,HOMO}}$ are very small or zero. The prescription for finding an energetically favourable deviation from the unfavourable pathway of Fig. 1, is as follows: Move the atoms into those different regions of space which are characterized by a large functional value of $\rho_{\mathrm{HOMO,HOMO}}$ and the same sign of the function [7].

Leaving the C- and O-atoms in place, we displace the nuclei along the trial pathway by increasing $R_{\mathrm{C-M}}$. Moving the F-atom towards its position in geometry $\boldsymbol{P}$, ($z = 3.0$, $y = 1.2$) brings it into a region of negative $\rho_{\mathrm{HOMO,HOMO}}$; only a slight deviation from the trial pathway would take this atom into a region of high negative functional values. Similarly, the O-atom can be drawn into one of the two regions with negative values by a relatively small displacement. Therefore, the change in the angle ∡OCF as a result of the motion of these two atoms should not be large. In contrast, a large shift of the H-atom along the direction of the arrow has to occur, in order for it to reach the region around the F-atom with high negative functional values (see Fig. 3). Such a deviation from the trial pathway leading from ***R*** to ***P***, would be expected to produce a substantial decrease of the H—F distance, the C—H distance increasing only slightly.

These qualitative conclusions are substantiated by the calculations of Morokuma et al., who determined the most favourable pathway for the thermal decomposition of OCHF into CO and HF [8, 9]. They found the reaction pathway to be planar but highly asymmetrical. The deviation from the trial pathway suggested by Fig. 3 is compatible with the calculated geometry of the transition state [9]. Only a small increase of the OCF angle from 122° to 123.5° is found when the equilibrium nuclear configuration is compared with the transition state geometry. The major difference between them is in the position of the hydrogen atom. In the equilibrium geometry the ∡OCH angle is 127.7° [9] but it is increased to 187.3° in the transition state. The increase of the C—F bond distance from 1.357 Å to 1.867 Å is accompanied by only a small change in the C—H distance from 1.071 Å to 1.123 Å [9]. Thus, the location of the H-atom in the transition state agrees qualitatively with the large lateral displacement indicated in Fig. 3.

The observation that photochemical decomposition of formyl-fluoride leads to HF infrared laser emission [13] implies significant involvement of a change in the HF bond length during the fragmentation process. It is consistent with our analysis provided that, in analogy with the fragmentation of formaldehyde, it is preceded by internal conversion of excited OCHF to its ground electronic state. This possibility has indeed been considered by Klimek and Berry [13].

4. Conclusions

The qualitative agreement between the form of the calculated decomposition pathway [8, 9] and the nuclear displacement suggested by $\rho_{\mathrm{HOMO,HOMO}}$ supports the expectation that the form of the overlap function between two orbitals, which intercorrelate but possess a small overlap integral, can be used in order to determine the direction of energetically favourable nuclear motions on a potential energy surface.

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