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Mechanism of 1,2-Migration in β-(Acyloxy)alkyl Radicals

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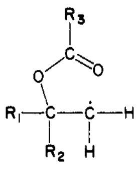
Abstract: Ab initio molecular orbital calculations using polarization basis sets and incorporating electron correlation have been used to examine the mechanism for 1,2-acyloxy migration in the prototype system, the β-(formyloxy)ethyl radical. The preferred pathway involves a five-membered cyclic transition structure which differs in geometric and electronic structure from the 1,3-dioxolanyl radical. The calculated transition structure resembles a loose complex between ethylenic and formyloxy fragments with considerable dipolar character. The higher barrier to rearrangement via the 1,3-dioxolanyl radical may be rationalized in terms of an intended but avoided crossing of electronic configurations.

Rearrangement of β-(acyloxy)alkyl radicals by 1,2-migration of the acyloxy group (e.g., **1** → **2**) provides a notable exception to the generalization that intramolecular homolytic reactions are direct analogues of intermolecular processes.[1] Consequently, it has attracted continuing attention[2-10] since its occurrence was first recognized by Surzur and Teissier[2] during homolytic addition to the acetate of 2-methylbut-3-en-2-ol. The rearrangement was independently reported by Tanner and Law,[3] who observed that the benzoyl peroxide catalyzed decarbonylation of 2-acetoxy-2-methylbutanal afforded a mixture of *tert*-butyl and isobutyl acetates. They attributed formation of the latter to the occurrence of the acetate migration (**1a** → **2a**) and suggested that the reaction proceeds through a 1,3-dioxolan-2-yl radical, **3a**, which "serves as a transition state or an unreactive intermediate".[3]

More detailed mechanistic studies were conducted by Beckwith and co-workers,[4,5] who used ^{18}O-labeled substrates to show that the rearrangement involves specific inversion of the two acyloxy oxygen atoms. Mechanisms involving elimination–addition or a three-membered cyclic transition structure could therefore be precluded. Generation of hydroxyl radicals in the presence of *tert*-butyl acetate in water gave ESR signals for both the rearranged and unrearranged radicals, **1a** and **2a**, but the putative intermediate, **3a**, could not be detected.[5] Conversely, similar treatment of the appropriate dioxolane gave **3a** but neither of the possible ring-opened products, **1a** and **2a**. It was concluded that the dioxolanyl radical, **3a**, does not lie on the reaction coordinate for the rearrangement (**1a** → **2a**), which must therefore proceed in concerted fashion through a cyclic transition structure (e.g., **4a**).[5]



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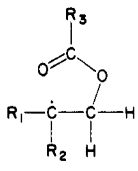

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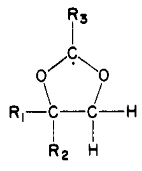

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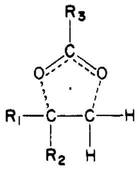

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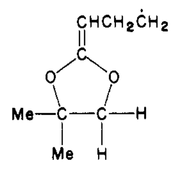

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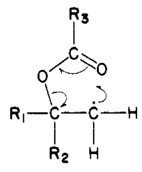

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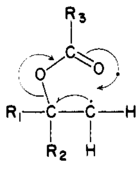

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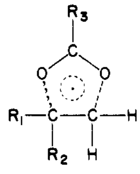

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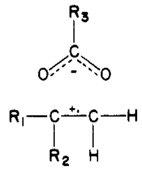

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a R$_1$, R$_2$, R$_3$ = Me

b R$_1$, R$_2$ = Me; R$_3$ = Ph

c R$_1$ = Ph; R$_2$, R$_3$ = Me

d R$_1$, R$_2$ = Me; R$_3$ = cyclopropyl

e R$_1$, R$_2$ = Me; R$_3$ = CF$_3$

Further support for this view was adduced from a kinetic study of the rearrangement of radicals generated by the tin hydride method.[5] As expected for a concerted process, rate constants were strongly affected by the nature of the substituents, R$_1$ and R$_2$, at the new radical center, but were relatively insensitive to the nature of R$_3$. Thus the rates of rearrangement[11] of radicals **1a** ($k_{75^\circ\mathrm{C}} = 3.2 \times 10^3\ \mathrm{s}^{-1}$) and **1b** ($k_{70^\circ\mathrm{C}} = 3.6 \times 10^3\ \mathrm{s}^{-1}$) are similar whereas that for the radical **1c** ($k_{70^\circ\mathrm{C}} = 1.3 \times 10^4\ \mathrm{s}^{-1}$) is considerably larger. If the dioxolanyl radicals **3a** and **3b** are on the reaction coordinate, the rates of rearrangement of **1a** and **1b** should be substantially different. Furthermore, attempts to generate dioxolanyl radicals by ring closure of *o*-acetoxyaryl radicals were unsuccessful.[6]

Despite this evidence, some doubts about the validity of the concerted mechanism remained, mainly because of inconsistencies in the various sets of kinetic measurements which were not made under identical experimental conditions.[7,8] A notable example is the observation that the ring opening of some dioxolanyl radicals (e.g., **3a** → **2a**) which cannot be detected in aqueous solution[4] proceeds more rapidly than the rearrangement **1a** → **2a** in organic solvents.[8] The question has recently been unambiguously resolved, however, by a study of some cyclopropyl-substituted species.[8] When the radical **3d** was generated in the cavity of an ESR spectrometer it underwent rapid ($k_{75^\circ\mathrm{C}} = 8.7 \times 10^5\ \mathrm{s}^{-1}$) opening of the cyclopropyl ring to give **5**. On the other hand, **1d** underwent the normal rearrangement to **2d** at a much slower rate ($k_{75^\circ\mathrm{C}} = 1.25 \times 10^2\ \mathrm{s}^{-1}$), and no trace of the product formed by ring opening of the cyclopropyl ring could be detected. Clearly, the dioxolanyl radical **3d** cannot lie on the pathway from **1d** to **2d**.

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Although the occurrence of a one-step concerted mechanism for the rearrangement of β-(acyloxy)alkyl radicals has thus been established, some important questions remain unanswered: namely, what is the nature of the transition structure for the rearrangement; how does it differ from a dioxolanyl radical; and why does it not collapse to dioxolanyl radical? An early response to these questions was the suggestion that geometric factors were of prime importance.[5] A cyclic transition structure such as **4** implies a planar disposition of the five annular atoms plus R_3, whereas the radical centers in 2-alkyl-1,3-dioxolan-2-yl radicals are known to be pyramidal.[4,12] More recently, however, 2-phenyl-1,3-dioxolanyl radical has been shown to be planar.[13] Consequently, geometric factors cannot be relevant, at least for benzoyloxy migration.

An early representation, **4**, of the transition structure[5] accommodates the idea that 1,2-acyloxy migration involves one-electron shifts as in **6**. Later, it was suggested[14] that the reaction could be viewed as an open-shell pericyclic reaction involving the electron shifts shown in **7** and that the transition complex was best visualized as **8** in which the circle represents a delocalized array of five electrons. This idea has recently been developed[8] to allow for the experimental observation that the rearrangement exhibits relatively large *A* factors and must, therefore, have a "loose" transition structure. Consequently, Ingold[8,9] has suggested that canonical structures such as **9** make an important contribution to the transition complex and so bestow dipolar character upon it. In striking confirmation of this hypothesis he has now shown that the radical containing the strongly electron-attracting CF_3 substituent rearranges almost 160 times more rapidly than its CH_3-substituted analogue.[9] This observation accords with the expectation that electron-attracting substituents at the 2-position should lower the energy of a dipolar transition structure.

Although the general nature of the transition structure is being revealed by such experiments, explicit details cannot be determined in this way and the questions raised above concerning the relationship of the transition structure to the dioxolanyl radical remain unanswered. Ab initio molecular orbital theory provides a means of obtaining such information. The detailed geometries of reactants and products and of transition structures for various possible reaction pathways can be determined, and the energy barriers for these pathways can be compared. We have such an approach here to study 1,2-migration in the prototype system, the β-(formyloxy)ethyl radical.

Table I. 3-21G Optimized Structures[a] for the β-(Formyloxy)ethyl Radical (**10**), 1,3-Dioxolanyl Radical (**11**), and Related Transition Structures (**12**, **13**)

	10	**11**	**12**	**13**
state (symmetry)	^2A (C_1)	$^2A_1$ (C_s)	$^2A_1$ (C_{2v})	^2A (C_1)
degrees of freedom[b]	24	13	8	24
C_1–C_2	1.496	1.558	(1.383)	1.512
C_2–O_3	1.466	1.453	2.033	1.482
O_3–C_4	1.345	1.397	1.257	1.374
C_4–O_5	1.200	(1.397)	(1.257)	1.304
O_5–C_1	(3.304)	(1.453)	(2.033)	(1.892)
C_1–H_6	1.071	1.077	1.068	1.070
C_1–H_7	1.072	1.078	(1.068)	1.074
C_2–H_8	1.080	(1.077)	(1.068)	1.077
C_2–H_9	1.079	(1.078)	(1.068)	1.077
C_4–H_{10}	1.076	1.071	1.082	1.073
$\angle C_1C_2O_3$	110.4	104.4	(102.2)	108.0
$\angle C_2O_3C_4$	118.5	109.2	104.6	110.1
$\angle O_3C_4O_5$	125.1	(109.3)	(126.4)	113.9
$\angle C_4O_5C_1$	(72.3)	(109.2)	(104.6)	(98.8)
$\angle O_5C_1C_2$	(55.6)	(104.4)	(102.2)	(91.5)
$\angle C_2C_1H_6$	120.6	112.7	120.6	118.5
$\angle C_2C_1H_7$	119.3	111.8	(120.6)	117.5
$\angle O_5C_1H_6$	(104.4)	108.0	91.1	(100.9)
$\angle O_5C_1H_7$	(112.0)	109.5	(91.1)	(105.6)
$\angle H_6C_1H_7$	(120.0)	(110.2)	(116.5)	(116.4)
$\angle C_1C_2H_8$	112.2	(111.8)	(120.6)	111.1
$\angle C_1C_2H_9$	111.2	(112.7)	(120.6)	113.3
$\angle O_3C_2H_8$	103.7	(109.5)	(91.1)	108.2
$\angle O_3C_2H_9$	109.1	(108.0)	(91.1)	105.7
$\angle H_8C_2H_9$	(109.9)	(110.2)	(116.5)	(110.4)
$\angle O_3C_4H_{10}$	109.7	115.2	116.8	115.6
$\angle O_5C_4H_{10}$	125.2	(115.2)	(116.8)	123.1
$\angle C_1C_2O_3C_4$	84.2	(−11.4)	(0.0)	16.4
$\angle C_2O_3C_4O_5$	2.2	(19.2)	(0.0)	17.5
$\angle O_3C_4O_5C_1$	(−27.7)	(−19.2)	(0.0)	(−35.4)
$\angle C_4O_5C_1C_2$	(60.9)	(11.4)	(0.0)	(39.7)
$\angle O_5C_1C_2O_3$	(−55.6)	(0.0)	(0.0)	(−30.5)
$\angle H_6C_1C_2O_3$	−142.5	(−116.9)	(−98.7)	−133.7
$\angle H_7C_1C_2O_3$	42.3	(118.3)	(98.7)	77.9

[a] Atom numbering as in Figure 1. [b] Nonindependent parameters are shown in parentheses.

Table II. 3-21G Optimized Structures[a] for the Formyloxy Radical (HCOO·) and Ethylene

	HCOO· $^2B_2$ (C_{2v})	HCOO· $^2A_1$ (C_{2v})		CH_2CH_2 ^1A_g (D_{2h})
C–O	1.255	1.225	C–C	1.315
C–H	1.074	1.143	C–H	1.074
∠OCO	113.7	140.6	∠CCH	121.9
∠HCO	(123.2)	(109.7)	∠HCH	(116.2)

[a] Nonindependent parameters are shown in parentheses.

Table III. Calculated Total Energies (hartrees)

	HF/3-21G	HF/6-31G	HF/6-31G*	MP2/6-31G
10	−264.70550	−266.06498	−266.19215	−266.55728
11	−264.68794	−266.03885	−266.16293	−266.52449
12	−264.64387	−266.00566	−266.12584	−266.52721
13	−264.64756	−266.00043	−266.11627	−266.48386
HCOO· ($^2B_2$)	−187.02849	−187.99404	−188.09215	−188.33585
HCOO· ($^2A_1$)	−187.01489	−187.98002	−188.07919	−188.33898
C_2H_4	−77.60099	−78.00438	−78.03169	−78.18197

Method and Results

Standard ab initio molecular orbital calculations were carried out by using a modified version[15] of the GAUSSIAN 80 system of programs.[16] Optimized equilibrium structures and transition structures were obtained with the split-valence 3-21G basis set[17] using gradient procedures.[16,18] In order to obtain more reliable relative energies, additional calculations were performed with the larger split-valence 6-31G basis set,[19] with the split-valence plus d-polarization 6-31G* set,[20] and with the incorporation of electron correlation using Møller–Plesset perturbation theory terminated at second order (MP2).[21,22] All calculations on open-shell systems employ the spin-unrestricted (UHF, UMP) formalism. Our best relative energies have been estimated by using the expression

$$\Delta E(\text{MP2/6-31G*}) \approx \Delta E(\text{MP2/6-31G}) + \Delta E(\text{HF/6-31G*}) - \Delta E(\text{HF/6-31G}) \quad (1)$$

This additivity approximation has been tested previously[23,24] and found to provide a useful approach when direct calculations em-

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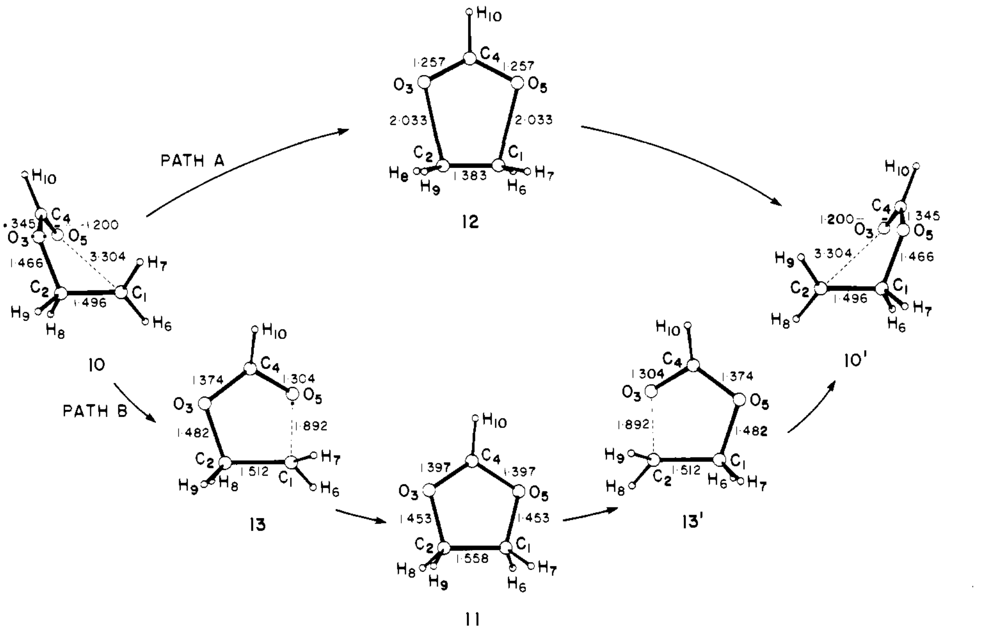

Figure 1. Schematic representation of equilibrium and transition structures on two pathways for the 1,2-migration in the β-(formyloxy)ethyl radical. Predicted values of important structural parameters are included.

Table IV. Calculated Relative Energies (kJ mol^{-1})

	HF/ 3-21G	HF/ 6-31G	HF/ 6-31G*	MP2/ 6-31G	MP2/ 6-31G*[a]
10	0	0	0	0	0
11	46	69	77	86	94
12	162	156	174	79	97
13	152	169	199	193	223
HCOO·($^2B_2$) + C_2H_4	200	175	179	104	108
HCOO·($^2A_1$) + C_2H_4	235	212	213	95	97

[a] Estimated by using eq 1.

ploying a polarized basis set *and* incorporating electron correlation are not feasible.

Calculations were performed for the β-(formyloxy)ethyl radical (**10**), the 1,3-dioxolanyl radical (**11**), the transition structure (**12**) for the 1,2-migration (**10** → **10'**) of the formyloxy group, the transition structure (**13**) connecting **10** and **12**, and finally the dissociation products, formyloxy radical (HCOO·) + ethylene. We should point out that the formyloxy radical has several low-lying electronic states which are close in energy. Quite sophisticated calculations are required to order and describe correctly the geometries (i.e., C_{2v} vs. C_s) of these states,[25] and we do not attempt to address this problem here. We have only examined the C_{2v}-constrained $^2A_1$ and $^2B_2$ states.

Optimized structural parameters for **10**–**13** are shown in Table I and for the dissociation products HCOO· and C_2H_4 in Table II. Corresponding total and relative energies are listed in Tables III and IV, respectively. The principal geometric changes occurring during the 1,2-migration are displayed in Figure 1 and a schematic energy profile is shown in Figure 2. Throughout this paper, bond lengths are in angstroms and bond angles in degrees.

Discussion

The β-(formyloxy)ethyl radical (**10**) is a conformationally flexible system allowing torsion about the C_1–C_2, C_2–O_3, and O_3–C_4 bonds. Smith and co-workers[26] have examined theoretically the conformational energy hypersurface in **10**, but their work suffers from the use of the INDO approximation and assued values of geometric parameters in the calculations. Previous work in the closely related ethyl formate molecule and on other alkyl formates[27] suggested to us a preferred ($C_2O_3C_4O_5$) cis arrangement about O_3–C_4 in **10** and that gauche and trans ($C_1C_2O_3C_4$) arrangements about C_2–O_3 might have comparable energies. Although it was not a central aim of the present study, we did explore some of these conformational possibilities.

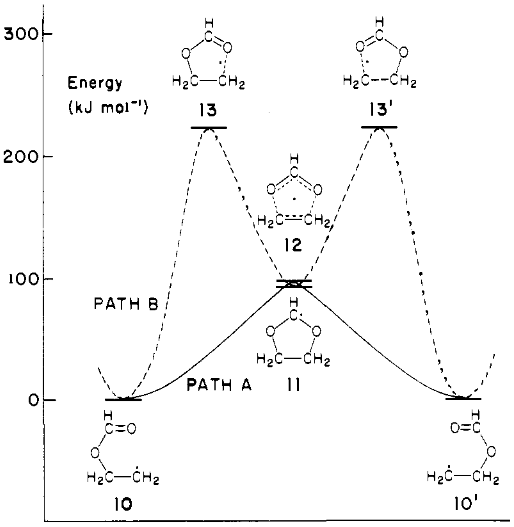

Figure 2. Schematic potential energy profiles for two pathways describing 1,2-migration (**10** → **10'**) in the β-(formyloxy)ethyl radical.

We find that the preferred conformation for **10**, the detailed structure of which is presented in Table I, has a near-cis arrangement (2.2°) about O_3–C_4, as expected, and a gauche arrangement (84.2°) about C_2–O_3. The torsion angles ($H_6C_1C_2O_3$ and $H_7C_1C_2O_3$) about C_1–C_2 are −142.5° and +42.3°, respectively, but previous experience[28] suggests that rotation about C_1–C_2 should occur relatively easily.

An alternative conformation with a cis arrangement about O_3–C_4 but trans about C_2–O_3 (i.e., with C_s symmetry) was also

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(25) See, for example: (a) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 4515. (b) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *Ibid.* **1983**, *105*, 1459.

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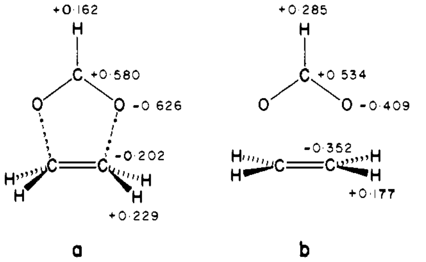

Figure 3. Calculated (HF/6-31G*) atomic charges in (a) transition structure **12** and (b) separated formyloxy radical and ethylene.

optimized and found to lie 2.2 kJ mol^{-1} above the cis-gauche form (**10**). Test calculations of distortions from the cis-trans conformation suggested that the cis-trans form is a local minimum on the potential surface.

Finally, an optimized structure was obtained for another conformation with C_s symmetry, this time with cis arrangements about both O_3–C_4 and C_2–O_3. This cis-cis form was found to lie 17.4 kJ mol^{-1} above **10** and to collapse to **10** when the C_s symmetry constraint was removed.

Rearrangement of the β-(formyloxy)ethyl radical (**10** → **10′**) via path A proceeds through transition structure **12**. The geometry of **12** was optimized under a C_{2v} symmetry constraint but **12** was demonstrated to be a true transition structure on the HF/3-21G surface by calculating its vibrational frequencies. As required, one imaginary frequency was found, corresponding to distortion in the direction of **10** (or **10′**). In addition, explicit calculation showed that **12** collapsed to **10** without a barrier.

The principal structural changes which take place in going from **10** to **12** are increases in the C_2–O_3 and C_4–O_5 lengths and decreases in C_1–C_2, O_3–C_4, and C_1–O_5. Structure **12** thus resembles a complex between ethylene and formyloxy radical in a $^2A_1$ state. Despite the long C–O bonds (2.033 Å) linking the HCOO· and CH_2CH_2 moieties in **12**, there are significant structural perturbations (notably a lengthening of the C=C and C–O bonds) compared with the separated species.

The predicted structure of **12** is consistent with the loose complex description suggested by Ingold[8] on the basis of the large *A* factors observed in his kinetics experiments. The calculations also support the suggestion[8,9] that there is considerable dipolar character in **12**. Thus, the HF/6-31G* charges evaluated by using the Mulliken approach[29] (Figure 3) show a charge transfer in **12** of approximately 0.5 electron in the direction $(CH_2CH_2)^{+\cdot}(HCOO)^-$ (cf. **9**). This is consistent with the observed[9] rate enhancement which results from CF_3 substitution in the formyloxy group and has obvious implications regarding the effect of substituents in the ethylenic moiety.

Our calculations show that, on the HF/3-21G surface at least, dissociation of **10** or of **12** to C_2H_4 + HCOO· ($^2A_1$) can proceed without reverse activation energy, i.e., is monotonically uphill. The energy requirement for such a dissociation decreases, however, at higher levels of theory with the result that at our best level of theory (MP2/6-31G* estimated by using eq 1), **12** and the dissociation products have similar energies. It has been found[30] that MP2 calculations frequently overestimate the correlation correction to relative energies and that calculations at higher levels often move back toward the Hartree-Fock results. It is likely, therefore, that **12** does lie lower in energy than the dissociation products.

Our best calculations predict a barrier of 97 kJ mol^{-1} for the 1,2-formyloxy migration via **12** (path A). They also predict that the barrier for dissociation-recombination is of similar magnitude. The latter result appears to conflict with the clear experimental evidence[5] for an intramolecular rearrangement, although the conflict is reduced when we recognize, as noted above, that at higher levels of theory the dissociation-recombination mechanism will be relatively disfavored. In addition, we note that the experimental results all refer to observations in solution and refer to substituted species. Both solvation and substituent effects are likely to stabilize the dipolar transition structure **12** relative to the nonpolar dissociation products and hence to favor the intramolecular pathway A over dissociation-recombination.

Rearrangement of the β-(formyloxy)ethyl radical (**10** → **10′**) via B proceeds through the transition structure **13** and the 1,3-dioxolanyl intermediate **11**. In this case, the C_1–C_2, O_3–C_4, and C_4–O_5 bonds all lengthen while C_2–O_3 and C_1–O_5 decrease in length. The resultant bonds in **11** resemble single bonds in length. Whereas the intermediate **11** and five-membered transition structure **12** have similar energies, the calculated barrier to rearrangement via path B (223 kJ mol^{-1}) is substantially greater than that via path A (97 kJ mol^{-1}).

How can the large difference between the barriers for paths A and B be rationalized? We begin by examining electronic configurations in a simplified version of the 1,2-formyloxy migration reaction in which all species have a plane of symmetry containing the non-hydrogen atoms. Our only task is to count the number of electrons of π-symmetry (a″ under C_s) in such species. For example, if we consider **10** in one of the conformations with a plane of symmetry (e.g., cis-cis), the number of electrons of π-symmetry is eight (four from the formyloxy moiety and two from each of the methylene groups, the odd electron being part of the σ-system). This is also the number of electrons of π-symmetry in **12**, and hence the ground-state electronic configurations of **10** and **12** correlate with one another. The (relatively) low barrier for rearrangement via path A follows. The $^2A_1$ electronic configuration of **12** also correlates with that of $^2A_1$ HCOO· + C_2H_4.

On the other hand, if the 1,3-dioxolanyl radical (**11**) is considered with C_{2v} symmetry, it would have nine electrons of π-symmetry. The ground-state configurations of **10** and **11** would then not correlate with one another. In fact, **10** and **11** have symmetry lower than assumed in this analysis, and the strict symmetry argument does not apply. However, it would be appropriate to say that there is an intended but avoided crossing of electronic configurations in path B linking **10** and **11**. Thus a barrier larger than for path A is expected and observed. In addition, the C_{2v} form of **11** correlates with a highly excited $^2B_1$ (five π-electron) state of HCOO· with the result that a reverse activation barrier would certainly be expected for dissociation of **11** (in contrast to **12**) to HCOO·($^2A_1$) + ethylene.

Finally, we note that the dioxolanyl radical **11** and the transition structure **12** differ markedly in geometric and electronic structure. Thus, **11** corresponds to a distorted π-radical (with nine electrons of π-symmetry under C_{2v}) while **12** corresponds to a σ-radical (with eight electrons of π-symmetry) and the two structures are separated by a symmetry-imposed barrier. The most striking geometric difference is the greatly elongated C–O length (for C_1–O_5 and C_2–O_3) in **12** compared with **11**.

Concluding Remarks

The main conclusion to emerge from this study is that, in agreement with conclusions drawn from previous experimental investigations, the preferred pathway for 1,2-formyloxy migration in the β-(formyloxy)ethyl radical involves a five-membered cyclic transition structure which differs in geometric and electronic structure from the 1,3-dioxolanyl radical. The calculated transition structure has long C—O bonds, i.e., may be described as loose, and also has considerable dipolar character. The higher barrier to rearrangement via the 1,3-dioxolanyl radical may be rationalized in terms of an intended but avoided crossing of electronic configurations. More refined calculations, notably geometry optimizations at correlated levels of theory, would be desirable but are prohibitively expensive at the present time for systems as large as the β-(formyloxy)ethyl radical. Although our quantitative results would undoubtedly be modified by such refinements, we are confident that our qualitative conclusions would still hold.

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