1,3-Sigmatropic Shifts in Carbonylketenes, Carbonyl Isocyanates and Analogous Compounds

Minh Tho Nguyen,*[a] Luc Landuyt,[a] and Hue Minh Thi Nguyen[a,b]

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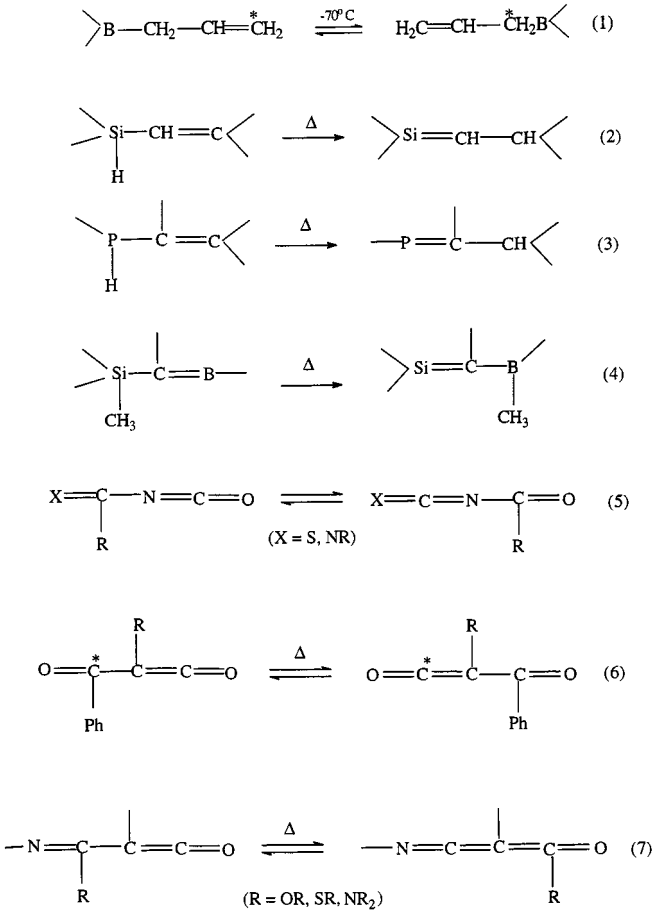
Antarafacial 1,3-sigmatropic shifts in carbonyl derivatives of ketenes, isocyanates, thioketenes and thioisocyanates have been studied by means of ab initio MO calculations. Energy barriers in 20 different systems have been uniformly determined at the MP4SDTQ/6-31G(d,p) level, based on MP2/6-31G(d,p) geometries and corrected for zero-point energies. For formylketene, higher-level calculations using the QCISD(T) method and larger basis sets [up to 6-311++G(2df,2p)] have also been carried out. In carbonylketenes, the migratory aptitude of the substituents R is established as follows: Cl > SH > NF_2 > NH_2 > BH_2 > PH_2 > F > OCH_3 > OH > SiH_3 > H > C_6H_5 > CH_3. The barrier heights range from 10 kcal/mol for Cl migration to 35 kcal/mol for phenyl migration. Several factors influencing the energy barriers including the existence of an n-electron pair at the migrating atom, its size, electronegativity and ability to adapt to a hypervalent state, as well as the strengths of the breaking and forming bonds have been examined in detail. Generally speaking, 1,3-sigmatropic rearrangements are feasible thermal unimolecular reactions even under mild experimental conditions.

Introduction

Many chemists associate 1,3-sigmatropic migrations in organic compounds in the gas phase with difficult, if not unachievable, chemical transformations. This is understandable as these molecular processes often require extremely high activation energies. For instance, the transition structure for the prototype 1,3-shift of the hydrogen in propene was calculated to lie close in energy to the C−H bond dissociation limit.[1] Allylic rearrangement involving migration of a carbon group, such as those of vinylcyclopropenes giving cyclopentenes and of vinylcyclobutenes giving cyclohexenes, also demand substantial activation energies that could be even larger than the C−C bond energies.[2] Nevertheless, a brief survey of the rather limited literature available on 1,3-sigmatropic rearrangements reveals that this mode of unimolecular reaction is achievable, even under moderate reaction conditions, by modifying one of the following factors: (i) the nature of the migrating group,[3,4] (ii) the nature of the terminal and central atoms,[5−9] or (iii) the electronic state of the substrate.[10−13] It is needless to say that, in solution, solvent molecules often exert an active catalytic effect, removing a great deal of the barrier height.[14] In this paper, we are mainly concerned with the first two factors. The migration in ionized states has been examined in some previous papers.[7,10−13]

While 1,3-shift of a methyl group in alkenes is virtually unknown, there are examples of this reaction mode involving instead the boryl, silyl and thio groups.[3] The most remarkable feature of reported results is perhaps the detection of a permanent 1,3-rearrangement in allylboranes (Equation 1), even at low temperatures.[4] In this system, the electron-poor boryl group is crossing continuously from one terminal carbon center to the other.



[a] Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium
E-mail: minh.nguyen@chem.kuleuven.ac.be
[b] Permanent address:
College of Education, Vietnam National University, Hanoi, Vietnam

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Regarding the terminal centers, the migratory process appears to be greatly facilitated by replacing first-row atoms by second-row atoms. For instance, cases of a 1,3-hydrogen migration in silapropene[5] (Equation 2) and phosphapropene[6][7] (Equation 3) have been reported. Similarly, some evidence for a 1,3-methyl shift along a BCSi skeleton[8] (Equation 4) has recently been presented.

Rearrangement of thioacyl and imino isocyanates, apparently involving a 1,3-migration of a substituent (Equation 5), was observed more than three decades ago by Goerdeler and co-workers.[15] The most compelling evidence yet for a similar migration in the gas phase perhaps comes from a study by Wentrup and Netsch[16] on carbonylketenes. By means of ^{13}C-labelling experiments, these authors demontrated the scrambling of a phenyl group upon warming of an acylketene (Equation 6).

Analogous reactions involving not only the migration of hydrogen or phenyl, but also that of the electron-rich alkoxy and alkylamino groups (Equation 7) have recently been reported.[17−19] Moreover, the successful competition of these 1,3-shifts with other possible reactions in these systems, such as 1,5-migrations or intramolecular [2+2] cycloadditions, suggests that activation energies of the former should not be inordinately large.

In a previous paper,[20] a molecular orbital study of the hydrogen scrambling in a prototype oxoketene (Equation 6, R = H) was reported. Using ab initio molecular orbital calculations at the partial fourth-order perturbation theory (MP4SDQ) level with the polarized 6−31G(d,p) basis set and a correction for zero-point energies, an energy barrier of 39.7 kcal/mol for the 1,3-hydrogen shift in formylketene was determined. A more recent theoretical study[21] using approximate QCISD(T) with the 6-311+G(2df,2p) basis set led to a value of 34 kcal/mol for this quantity. In fact, it is established that barrier heights for 1,3-shifts are consistently reduced upon extension of wavefunctions. In any case, the energy barrier for the 1,3-hydrogen shift in formylketene is only ca. 3 kcal/mol larger than for that in formic acid.[10] The migratory aptitude of a series of substituents in the oxoketene → oxoketene rearrangement has also been determined by calculations;[21] accordingly, the 1,3-migratory aptitude of a substituent is simply dependent on its ability to donate n electrons.

As part of our continuing theoretical study[7,10−12] on 1,3-sigmatropic rearrangements, we have extended it by investigating the migration of several typical substituents, including the boryl (BH_2), methyl (CH_3), amino (NH_2), hydroxy (OH), fluoro (F), silyl (SiH_3), phosphanyl (PH_2), thiohydroxy (SH) and chloro (Cl) groups. While the boryl group represents an electron-deficient substituent, NH_2, OH, PH_2, and SH represent electron-rich groups. This broad series of substituents allows a comparison to be made between the migratory aptitude of groups containing first-row and second-row atoms. To further approach the complexity of real systems, we have also considered carbonylketenes containing some larger groups, namely, methoxy (CH_3O), difluoroamino (F_2N) and phenyl (C_6H_5). Migration in a series of carbonyl isocyanates (Equation 5, X = O, R = H, F and Cl) as well as hydrogen migrations in analogous systems such as iminoketene[4] (Equation 7, R = H), thioformylketene (HC(=S)−CH=C=O), thioformylthioketene (HC(=S)−CH=C=S) and iminoketenimine (HN=CH−CH=C=NH) have also been investigated in order to determine the influence of the central and terminal atoms on the migrating process. An objective was to quantify the migratory ability of the different substituents and to understand the order of the relative abilities.

Details of Calculations

Geometrical parameters of stationary points were initially optimized at the Hartree−Fock (HF) level with the 3-21G(d) basis set.[22] Harmonic vibrational analysis was carried out at this level [HF/3-21G(d)] in order to characterize the stationary points located. Then, the geometries of the relevant equilibrium and transition structures were refined at the second-order Møller−Plesset perturbation theory level (MP2)[24] using the dp-polarized 6-31G(d,p) basis set.[22] Uniformly improved barrier heights were obtained through single-point electronic energy calculations based on MP2/6-31G(d,p)-optimized geometries, that incorporate correlation energy at the full fourth-order perturbation theory level [MP4SDTQ/6-31G(d,p)]. For the unsubstituted formylketene, calculations using a larger basis set and quadratic configuration interaction methods were also carried out. Finally, localized orbitals obtained according to the Boys method[23] were calculated using HF/6-31G(d,p) wavefunctions. Throughout this paper, bond lengths are given in angstrom, bond angles in degrees, total energies in hartree, zero-point vibrational and relative energies, unless otherwise stated, in kcal/mol. All calculations were carried out using the Gaussian 88 program.[24]

Results and Discussion

1,3-Hydrogen Shift in Unsubstituted Formylketene

In order to calibrate calculated results for larger systems, we first made a comparison of data obtained for the simplest oxoketene using different computational methods. Results summarized in Table 1 confirm that the barrier height for antarafacial 1,3-H shift decreases upon extension of the atomic functions. Nevertheless, extension beyond the 6-311++G(d,p) basis seems not to induce any further significant reduction of the barrier. On the other hand, the perturbational MP4SDTQ values are smaller than the corresponding quadratic configuration interaction, QCISD(T), values. Within each basis set, the perturbation series is not well-converged at lower order; therefore the MP3 values, as employed by Wong and Wentrup,[21] are markedly overestimated. In addition, corrections due to triple substitutions play a crucial role in reducing the barrier. Overall, the barrier height under consideration could be estimated as 33 ± 3 kcal/mol, in agreement with a previous study.[21] Such an energy barrier is rather small compared with that

of about 80 kcal/mol in propene, but is comparable with those in amidine ($H_2N-CH=NH$), formic acid ($HO-CH=O$) and phosphapropene ($H_2P-CH=PH$).[7−11] Owing to the presence of oxygen, the electron-deficient character of the C=O carbon atom is reinforced and stabilized by delocalization, thereby making it more able to capture the migrating atom.

The decreased barrier is also caused by the weakened C−H bond. A formyl C−H bond is apparently weaker than that in hydrocarbons. The transition state structure for a 1,3-H shift in formylketene is also less compact, giving rise to smaller angular distortions. The calculated results (Table 1) also suggest that perturbation MP2 or MP4SDTQ calculations with the 6-31G(d,p) basis set provide sufficiently good estimates for the barrier; therefore we have considered only these levels of accuracy for larger systems.

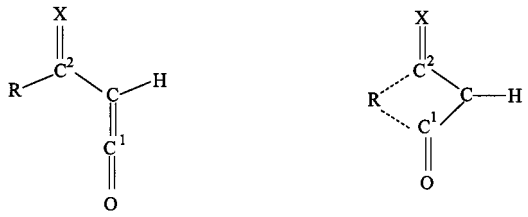
Table 1. Calculated barrier height for the antarafacial 1,3-hydrogen shift in formylketene

Method	Total energy[a]	Barrier height[b]
HF/6-31G(d,p)	−264.45401	53.0
MP2/6-31G(d,p)	−265.19251	32.9
MP3/6-31G(d,p)	−265.19122	42.3
MP4SDTQ/6-31G(d,p)	−265.24584	31.0
CISD/6-31G(d,p)	−265.08860	45.0
CISDQ/6-31G(d,p)	−265.20731	40.4
QCISD/6-31G(d,p)	−265.21061	40.0
QCISD(T)/6−31G(d,p)	−265.23770	36.0
MP2/6-311++G(d,p)	−265.31884	31.7
MP3/6-311++G(d,p)	−265.31096	40.8
MP4SDTQ/6−311++G(d,p)	−265.37682	29.7
QCISD/6-311++G(d,p)	−265.33227	38.2
QCISD(T)/6−311++G(d,p)	−265.36680	34.0
MP2/6-311++G(2d,p)	−265.37306	31.5
MP2/6-311++G(2df,2p)	−265.45608	31.2

[a] Total energy of formylketene based on MP2/6-31G(d,p)-optimized geometries given in Table 2. Core orbitals are frozen. − [b] Including zero-point vibrational energies (ZPE).

Migration in Carbonylketenes

Each carbonylketene could in principle exist in two distinct *s-cis* and *s-trans* configurations. The relative energies of these are largely dependent upon the substituents.[21] Here, we consider only the *s-trans* configuration, which has an appropriate nuclear disposition for a 1,3 shift of the substituent on the carbonyl moiety. Regarding the transition state, only structures for antarafacial migration have been found. While the ketene structures investigated are depicted in Scheme 1, selected geometrical parameters determined at the MP2/6-31G(d,p) level for equilibrium structures are given in Table 2, calculated total and zero-point vibrational energies are collected in Table 3, and barrier heights are listed in Table 4. As the MP2/6-31G(d,p) geometries for formylketene system are not significantly different from the MP2/6-31G(d) results reported in ref.[21], geometries of the transition structure are omitted to simplify the presentation of data. For the sake of convenience, results obtained for other systems are also given in Tables 2, 3 and 4, although these will be discussed in following sections.



Carbonyl ketene (M) TS for antarafacial 1,3-R shift

Scheme 1. Equilibrium (M) and transition (TS) structures of systems considered

Regarding the barrier heights for 1,3-migration of the groups considered, the following sequence can be established: Cl < SH < NF_2 < NH_2 < BH_2 < PH_2 < F < OCH_3 < OH < SiH_3 < H < C_6H_5 < CH_3. Whenever a comparison in possible, this order is in agreement with that previously found by Wong and Wentrup.[21] In addtion, a number of statements can be made:

(i) Relative to hydrogen, only phenyl and methyl groups require larger activation energies. Except for BH_2 and SiH_3, the remaining groups possess n-electron pairs.

(ii) With the exception of the phosphanyl group, substituents containing second-row atoms generally have a larger migratory aptitude than their first-row isovalent counterparts. Of the simple substituents, chloro is thus associated with the smallest energy barrier, about 11 kcal/mol, followed by the mercapto group (SH). In view of the fact that chloro is a weaker π-donor than fluoro and mercapto a weaker π-donor than hydroxy, the obtained results clearly suggest the unimportance of π-substituent orbitals in the antarafacial 1,3-shift. This is also in line with the corresponding C−R bond energies, which are expected to have an important influence on the barrier height. In fact, the C−R bond becomes consistently weaker when R contains a second-row atom.

(iii) NF_2 is a better migrating group than NH_2. Similarly, OCH_3 is better migrating group than OH. Thus, σ-donor groups tend to favour the migration by reinforcing the electron density around the migrating atom. An analysis of the localized molecular orbitals (LMO) in the transition-state structure for H migration using the Boys procedure suggests that there is actually a high electron density around the migrating hydrogen which moves, according to the LMO picture, as a hydride anion. The migration can thus be viewed as a swing of a negative group between two positive termini. As a consequence, the stronger the electrostatic interaction, the faster the migration and the smaller the barrier. There appears to be a certain non-linear relationship between the unpaired electron density of the moving group and the barrier height. Another influencing factor is that second-row atoms are less electronegative than first-row atoms but their more voluminous size accommodates more easily the loosely bound transferring electrons. In ref.[21], a stabilizing donor-acceptor interaction between the substituent lone

Table 2. Selected MP2/6-31G(d,p)-geometrical parameters of the equilibrium structure RC=X−HC=C=O considered[a]

Structure, X/R	$C=C^1$	$C^1=O$	C^1-C^2	$C^2=X$	C^2-R	C^1-R	C^1CC^2	RC^2C	CC^2X
1, O/H	1.332	1.173	1.458	1.225	1.154	2.600	120.0	121.5	123.4
2, O/BH_2	1.334	1.173	1.467	1.245	1.595	−	122.3	120.4	119.6
3, O/CH_3	1.330	1.175	1.471	1.228	1.513	2.885	122.1	117.5	120.4
4, O/NH_2	1.327	1.175	1.478	1.226	1.384	2.795	121.5	115.0	123.1
5, O/OH	1.331	1.171	1.456	1.217	1.367	2.629	120.4	111.3	125.5
6, O/F	1.334	1.169	1.445	1.199	1.378	2.574	119.2	110.1	128.7
7, O/SiH_3	1.333	1.173	1.465	1.240	1.920	3.294	122.8	124.0	120.0
8, O/PH_2	1.331	1.173	1.466	1.229	1.873	3.167	123.1	119.7	125.7
9, O/SH	1.331	1.172	1.460	1.220	1.805	3.007	123.3	115.3	122.5
10, O/Cl	1.336	1.168	1.443	1.204	1.810	2.904	121.8	113.0	126.3
11, O/OCH	1.331	1.172	1.459	1.218	1.364	2.611	120.1	110.7	125.3
12, O/NF_2	1.337	1.168	1.443	1.213	1.442	2.895	126.2	118.8	126.2
16, NH/H	1.330	1.175	1.460	1.285	1.088	2.624	120.9	116.7	127.3
17, S/H	1.337	1.172	1.435	1.632	1.089	2.585	120.4	119.8	124.8

[a] See Scheme 1 for atom numbering.

pair and the vacant orbital of the ketene moiety was proposed in order to account for the substituent behaviour. Such a view is certainly valid and complements the simple view based on the charge distribution discussed above.

(iv) Regarding phosphanyl (PH_2), its migratory capacity is much smaller than of amino. The corresponding LMO picture shows a significant displacement of electron pairs toward C atoms.

(v) The fact that F is a better migrating group than OH, but that NH_2 is better than both OH and F demonstrates that electronegativity is important but not the predominating factor. The ability of nitrogen to exist in a tetracoordinated state undoubtedly induces a greater stabilization of the transition structure. Hypervalency is also likely to be the main reason for the contrasting behaviour of methyl and silyl. Indeed, a pentacoordinated carbon atom is highly destabilized, whereas a pentacoordinated silicon atom is a more commonly encountered phenomenon.

(vi) Phenyl migration requires an energy barrier slightly larger (by 2.4 kcal/mol) than that for an H shift, but much smaller than that for methyl migration (by 13.4 kcal/mol). Other factors seem to intervene in this case since the relative C−H and C−C bond energies are not favourable for C migration. In a perpendicular conformation, the sp^2-carbon atom of the phenyl ring that adopts a normal tetravalent state in the transition structure can use two opposite lobes of its p orbital to interact with both of the terminal carbon atoms. This feature clearly makes phenyl migration more favourable than methyl migration. The barrier height for phenyl migration amounts to about 35 kcal/mol. Experimentally, phenyl migration in benzoylketene has been observed at high temperature (Equation 6). Under flash-vacuum pyrolysis conditions, phenyl migration was noticed at 550°C and was complete at 750°C.[16] Hence, observation of unimolecular 1,3-migration of all the groups considered above, except perhaps for CH_3, should be possible under even milder experimental conditions than these.

(vii) The behaviour of boryl is rather intriguing in view of the fact that it moves quasi-freely in vinylboranes (Equation 1). Thus, a large increase in barrier height actually occurs upon replacement of terminal CH_2 moieties by C=O. Boron is an electron-deficient element and LMO analysis suggests that BH_2 migrates as a cation between two negatively charged termini. Due to the presence of O, the nucleophilic character of C(=O) is reduced relative to the CH_2 analogue, and hence the transition structure becomes less stabilized and the barrier is increased.

In summary, a number of factors influencing the migratory aptitude of substituents in 1,3-migration have been identified: existence of an n-electron pair at the migrating atom, its size and electronegativity, its ability to accommodate hypervalency in the transition structure, and the relative strengths of the breaking and forming bonds. Any factor which reinforces the electron density around the migrating atom is expected to favour the sigmatropic rearrangement. Low barrier heights calculated for electron-rich groups such as SR, OR, Cl… are consistent with their facile migrations observed experimentally in analogous systems.

Migration in Carbonyl Isocyanates

We have considered only three simple migrations involving hydrogen, fluorine and chlorine. Geometrical parameters of the transition state structures are given in Scheme 2. The equilibrium structures have been extensively investigated in an earlier study.[26] Energies are summarized in Tables 2−4 (reactions 14, 15 and 16). Two remarkable results can be noted:

(i) An energy-barrier ordering similar to that in carbonylketenes has been found, Cl < F < H. The transition-state structure becomes looser and angular deformation at the central nitrogen atom thus becomes smaller in the same sequence.

(ii) The barriers for 1,3-migration are consistently higher in isocyanates than in ketenes. The difference obviously arises from the central atom, which is nitrogen in isocyanates and carbon in ketenes. This can simply be understood by applying the charge model discussed above. In the four-membered ring transition structures (Scheme 2), a large delocalization of the nitrogen lone pair occurs, partially neutralizing the positive charge on the carbon atoms. This, in

Table 3. Total and zero-point vibrational energies of the species considered

Systems[a]		MP2/6-31G (d,p)[b]	MP4SDTQ/ 6-31G(d,p)[c]	ZPE[d]
I. Carbonylketenes RC(=O)−CH=C=O				
1, R = H	M	−265.21314	−265.24584	26.4
	TS	−265.15560	−265.19129	23.2
2, R = BH_2	M	−290.53521	−290.57744	32.6
	TS	−290.50387	−290.55004	31.2
3, R = CH_3	M	−304.41080	−304.45477	48.0
	TS	−304.33028	−304.37598	46.1
4, R = NH_2	M	−320.44497	−320.48378	37.1
	TS	−320.42125	−320.45887	36.9
5, R = OH	M	−340.28833	−340.32218	29.7
	TS	−340.24611	−340.28049	28.3
6, R = F	M	−364.25704	−364.28834	22.3
	TS	−364.22519	−364.25911	21.3
7, R = SiH_3	M	−555.39218	−555.43275	35.6
	TS	−555.34462	−555.38894	34.2
8, R = PH_2	M	−606.63262	−606.67329	31.5
	TS	−606.60543	−606.64451	31.0
9, R = SH	M	−662.87041	−662.90762	26.3
	TS	−662.84868	−662.88708	25.3
10, R = Cl	M	−724.26261	−724.29624	21.1
	TS	−724.24269	−724.27779	20.3
11, R = OCH_3	M	−379.46120	−379.50812	46.8
	TS	−379.42597	−379.47263	45.5
12, R = NF_2	M	−518.31702	−518.36490	26.5
	TS	−518.29362	−518.33995	25.4
13, R = C_6H_5	M	−495.53067		76.5
	TS	−495.47175		74.9
II. Carbonyl isocyanates RC(=O)−N=C=O				
14, R = H	M	−281.27214	−281.30013	19.3
	TS	−281.18606	−281.21789	16.1
15, R = F	M	−380.30637	−380.33326	15.4
	TS	−380.26265	−380.29298	14.3
16, R = Cl	M	−740.31177	−740.34100	14.2
	TS	−740.27787	−740.30976	13.4
III. Other systems				
17, HC(=O)−CH=C=NH	M1	−245.35501	−245.39249	33.3
	TS	−245.28413	−245.32372	29.6
HC(=NH)−HC=C=O	M2	−245.36357	−245.40123	33.9
18, HC(=O)−CH=C=S	M1	−587.80193	−587.83704	24.9
	TS	−587.74225	−587.77967	21.9
HC(=S)−CH=C=O	M2	−587.80914	−587.84302	25.2
19, HC(=NH)−CH=C=NH	M	−225.50648	−225.54895	40.9
	TS	−225.39340	−225.43468	35.3
20, HC(=S)−CH=C=S	M	−910.39951	−910.43548	23.7
	TS	−910.33549	−910.37357	20.5

[a] Using MP2/6-31G(d,p) geometries, except for C_6H_5, which is based on HF/6-31G(d,p) geometries. – [b] Full sets of MOs are employed. – [c] Core orbitals are frozen. – [d] Zero-point energies from HF/3-21G (d) calculations are scaled by a factor of 0.9.

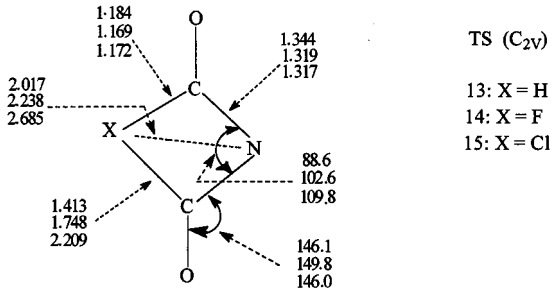
turn, reduces the stabilizing electrostatic interaction between termini and the migrating group, and as a consequence the energy barrier increases.

We also note that the donor-acceptor interaction mode[21] can also be used to interpret the calculated results. Isocyanates usually have high-lying unoccupied orbitals. The LUMO of HN=C=O is in fact higher in energy than that $H_2C=C=O$, thus implying a weaker interaction with n electrons of the migrating group in isocyanates than in ketenes.

Table 4. Calculated energy barriers for 1,3-migrations of the groups considered; X = CH, N; Y = O, NH, S; R = H, BH_2, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, NF_2, OCH_3, C_6H_5

System	MP2/6-31G (d,p) + ZPE	MP4/6-31G (d,p) + ZPE
I. Carbonylketenes RC(=O)−CH=C=O		
1, R = H	32.9	31.0
2, R = BH_2	18.2	15.8
3, R = CH_3	48.7	47.6
4, R = NH_2	14.6	15.4
5, R = OH	25.1	24.8
6, R = F	19.0	17.4
7, R = SiH_3	28.4	26.1
8, R = PH_2	16.5	17.5
9, R = SH	12.6	11.9
10, R = Cl	11.8	10.8
11, R = OCH_3	20.8	21.0
12, R = NF_2	13.6	14.6
13, R = C_6H_5	35.3	
II. Carbonyl isocyanates RC(=O)−N=C=O		
14, R = H	50.8	48.4
15, R = F	26.3	24.2
16, R = Cl	20.5	18.8
III. Other systems		
17, HC(=O)−CH=C=NH	45.6	44.3 (4.9)[a]
18, HC(=O)−CH=C=S	38.6	36.5 (3.5)[a]
19, HC(=NH)−CH=C=NH	65.3	66.1
20, HC(=S)−CH=C=S	36.9	35.6

[a] In parentheses are the energy differences between both equilibrium structures relative to the ketene forms.



Scheme 2. Transition structures in carbonyl isocyanates

Hydrogen Migration in Keteninines and Thioketenes

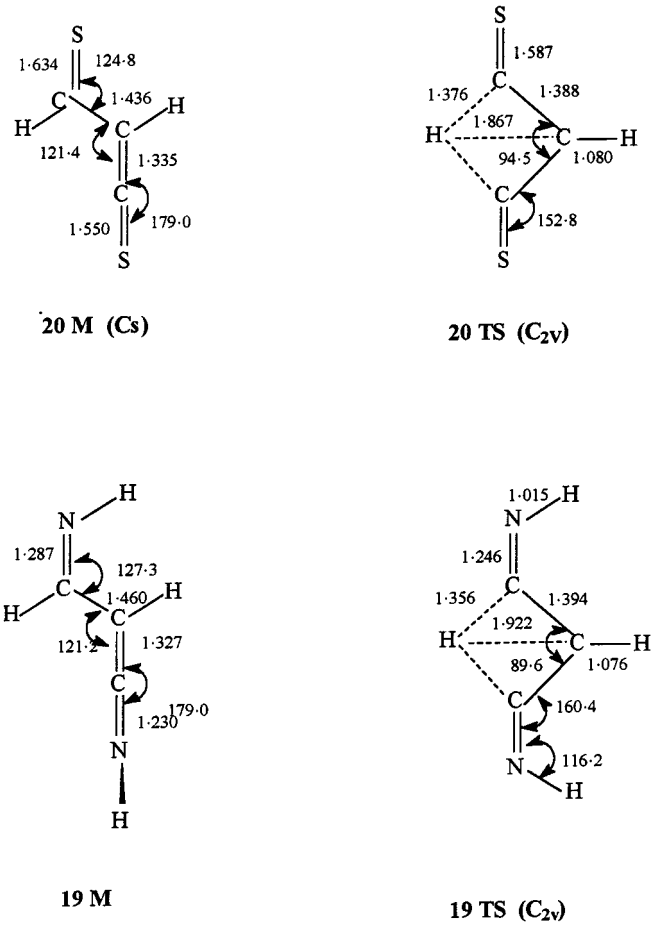
Finally, we have considered migrations in two asymmetric systems, formylketenimine (reaction 17, Tables 2−4) and formylthioketene (reaction 18) and two symmetric systems (Scheme 3), imidoylketenimine (reaction 19) and thioformylthioketene (reaction 20). A few interesting points emerge from the calculated results:

(i) Replacing O by S or NH systematically increases the barrier for 1,3-H shifts.

(ii) The markedly higher barrier in ketenimines is most likely due to the strained conformation of nitrogen in the transition structures. As seen in Scheme 3, imidoylketenimine possesses a perpendicular geometry in the equilibrium structure **19M,** but a planar geometry in the transition structure **19TS**. Distortion toward planarity is an energetically costly process. While 1,3-H migration in imidoylketenimine is not expected to be operative, there are experimental

indications for this rearrangement in imidoylketenes (reaction 7). Imidoylketene is in fact calculated to be less stable by about 5 kcal/mol than formylketenimine (Table 4, reaction 17). Proceeding from imidoylketene, the barrier height for a 1,3-H shift amounts to 39.4 kcal/mol (MP4SDTQ values), a value not inconsistent with the fact that experimental flash-vacuum pyrolysis has been carried out at 400−850°C. As mentioned in the introduction, facile migration of mercapto and amino groups has been observed in imidoylketenes.[17−19]

(iii) In thio compounds, the barrier height is slightly increased: S is less electronegative than O and thus induces a less positive carbon center. The 1,3-H shift in the all-sulfur system requires about 4−5 kcal/mol more activation energy than in the all-oxygen counterpart. Thioformylketene is found to be less stable than formylthioketene (Table 4, reaction 18). Starting from thioketene, the barrier is about 2 kcal/mol larger than that in formylketene.



Scheme 3. Equilibrium (M) and transition (TS) structures in thioformylthioketene (**20**) and imidoylketenimine (**19**)

To sum up in the present theoretical study, we have examined antarafacial 1,3-sigmatropic migrations in twenty systems analogous to formylketene. The migratory aptitude of the substituent R is established in the following sequence: Cl > SH > NF_2 > NH_2 > BH_2 > PH_2 > F > OCH_3 > OH > SiH_3 > H > C_6H_5 > CH_3. The factors influencing the energy barrier include the existence of an n-electron pair at the migrating atom, its size, electronegativity and ability to adapt to a hypervalent state in the transition structure, as well as the relative strengths of the breaking and forming bonds. With the exception of BH_2, the most crucial factor is perhaps the aptitude of R to accommodate a high electron density; the greater the negative charge, the lower the barrier. Central and terminal atoms also play an important role. While nitrogen in the central position disfavours the migration, any other electronic factor which stabilizes the positive charge at the terminal atom is expected to favour the process. Steric deformation also tends to enlarge the barrier. Thus, replacement of O in ketenes by S or NH results in an increase of the barrier height. Overall, the aptitude of substituents R to undergo 1,3-sigmatropic migration can readily be rationalized in terms of a simple charge-distribution model in which R normally migrates as an anionic entity. Calculated results thus demonstrate that 1,3-sigmatropic rearrangements are quite feasible thermal unimolecular reactions, even under mild experimental conditions.

After submission of this paper, several experimental and theoretical studies[27−36] have been reported in the literature, in particular the work of Wentrup and co-workers[27−33] and Birney and co-workers,[34] dealing with the 1,3-sigmatropic rearrangements of acylketenes and related cumulene compounds involving different substituents such as dimethylamino, methoxy, thiomethoxy and chlorine. The 1,3-shift of the silyl group in allylsilane has also been investigated theoretically.[35,36] Wherever a comparison is possible, our calculated results are in good agreement with the reported observations. For example, the 1,3-shift of chlorine has been found to be a facile process, with a free energy of activation of 10 kcal/mol. Our calculations suggest in fact an energy barrier of 10.8 kcal/mol for the Cl migration in chlorocarbonylketene (cf. Table 4). This lends an additional support for the present evaluation of energy barriers.

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