in absorbance of 1,8-bis(dimethylamino)naphthalene (proton sponge) accompanying protonation by HCl produced in the reaction.[37] Excess of substrate was used to give zero-order kinetics and reasonable linearity of plots of absorbance against time were obtained. The second-order rate constant 1.8×10^{-5} M^{-1} s^{-1} was based on measurements at several substrate concentrations in the range $0.5–2.5 \times 10^{-3}$ M, and was derived from the expression $k = \Delta A/(\Delta t\epsilon[S])$, where $\Delta A/\Delta t$ is the slope of the plot of absorbance against time, ϵ is the extinction coefficient of the proton sponge, and [S] is the concentration of substrate; the initial concentration of proton sponge was 10^{-5} M.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We thank Frances Martin for experimental assistance.

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An ab Initio Study of the Cyclization and Rearrangement of Vinyl-, Imidoyl-, and Formylketene

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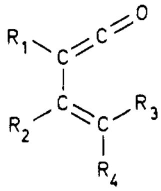
The 1,4-cyclization was studied in three model systems; formylketene, imidoylketene, and vinylketene, using ab initio MO methods. Structures of stationary points on the reaction potential energy surfaces were located at the HF/6-31G** level. Relative energies, estimated at the MP4SDQ/6-31G** level together with zero-point contributions, are as follows (in kcal/mol): formylketene (-17) → TS(4) → oxetone (0); imidoylketene (-10) → TS(15) → azetinone (0); and vinylketene (0) → TS(31) → cyclobutenone (0). The ring-opening of cyclobutenone is energetically more favorable than that of cyclobutene. The electronic reorganization accompanying the ring-closure of substituted ketenes was also examined using a localized orbital analysis. The process is found to be similar to the 1,5-cyclization of vinylazide and imidoylazide. Finally, the ketoketene–ketoketene rearrangement, including migration of a hydrogen in the formylketene, was considered. This 1,3-hydrogen shift is calculated to be a quite difficult chemical process requiring a large activation energy (even larger than that in formic acid).

1. Introduction

Vinylketenes **1** have been shown to be intermediates in several thermal and photochemical reactions of cyclobutenones **2**, and the ring–chain tautomerization reactions **2** → **1** have been extensively studied.[1,2] From a mechanistic point of view, the electrocyclic ring-opening of cyclobutenones **2** resembles, in many aspects, that of cyclobutenes.[3] In contrast, relatively little is known about the tautomeric equilibria either between imidoylketenes **3** and azetinones **4** or between acylketenes **5** and oxetones **6**. The oxetones and azetinones possess the additional feature that resonance of the carbonyl group leads to formally antiaromatic structures.



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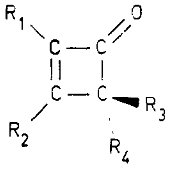

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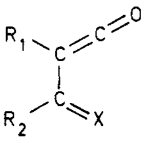
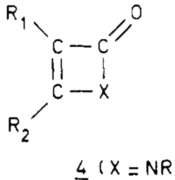


3 (X = NR)

5 (X = O)



4 (X = NR)

6 (X = O)

Azetinones **4** have been considered as potential intermediates in the nucleophilic ring-opening of β-lactams. Although these structures have occasionally been proposed in the literature[4] and are well-characterized in their benzo-fused forms,[5] the best evidence of their existence probably comes from either the base-catalyzed rearrangement of penicillins to thiazepinones[6] or the treatment of isoxazoles with tertiary amines and nucleophiles.[7]

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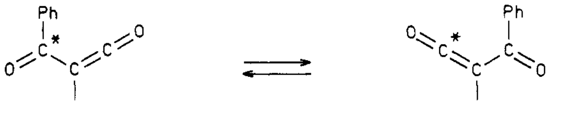
Table I. Geometries of Six Stationary Points Involved in the Rearrangement and Ring-Closure of Formylketene Optimized at the HF/6-31G Level**[a]

parameter	7 (cis)	8 (trans)	9 (ring)	10 (TS1)	11 (TS2)	12 (TS3)
C1-C2	1.327	1.321	1.490	1.305	1.383	1.420
C1-C3	1.460	1.463	1.322	1.506	1.383	1.365
C2-O	1.132	1.136	1.163	1.143	1.151	1.138
C3-O4	1.194	1.190	1.382	1.183	1.151	1.278
C2-O4	2.781		1.413			1.756
C1-H	1.072	1.072	1.066	1.074	1.071	1.066
C3-H	1.093	1.094	1.069	1.094		1.077
∠C1C2O	179.3	179.5	142.6	179.9	153.6	155.5
∠C3C1C2	118.7	120.5	85.0	122.6	94.4	91.0
∠O4C3C1	124.6	123.4	99.0	123.6	153.6	106.2
∠HC1C2	117.9	118.2	136.4	117.5	132.8	130.4
∠HC3C1	114.1	115.6	139.9	115.6		131.5
∠O4C3C1C2	0.0	180.0	0.0	89.9	180.0	0.0
C_iH_m					1.976	

[a] Numbering of atoms is given in Scheme I.

Whereas kinetic observation for the ring–chain tautomerization of benzoazetones have been reported,[8] the corresponding equilibria 4 ⇌ 3 have only theoretically been investigated by MNDO calculations.[9] Nevertheless, it is well-known that this semiempirical MO method tends to overestimate the ring stabilities compared with their open-chain isomers.[10]

With regard to the oxygen series 5 ⇌ 6, it has been shown that acylketenes 5 do not cyclize to oxetones 6 in the gas phase but instead dimerize.[11] This suggests that the rings 6 are thermodynamically less stable than the open forms 5. In addition, labeling experiments[12] have demonstrated that acylketenes 5 can undergo carbon scrambling via the 1,3-shift of a phenyl group at high temperature (>400 °C) (eq 1). This result is of interest since the 1,3-sigmatropic shift in neutral molecules is usually a quite difficult chemical process requiring a large activation energy.



5 (R_2 = Ph) (1)

In view of the scarcity of reliable quantitative information on these interesting processes and also as a preliminary to further experimental and theoretical studies of the involvement of azetinones 3 in the transformations of β-lactams,[13] we have carried out ab initio molecular orbital calculations on the three prototype electrocyclic ring-closures of the vinyl-, imidoyl-, and formylketene molecules as well as the simplest model ketoketene–ketoketene rearrangement involving the formylketene species.

2. Details of Calculations

Two basis sets have been employed in this work. The first consists of the split-valence 3-21G set,[14] and the second basis set is the dp-polarization 6-31G** set.[15] Geometries of stationary points were optimized at the single determinantal HF level with both basis sets. Harmonic vibrational frequencies were computed at the HF/3-21G level in order to characterize stationary points (as minima and transition structures) and to estimate the zero-point energy contributions to the relative energies between stationary points. The latter quantities were computed with values obtained by the Møller–Plesset perturbation theory[16] terminated at fourth-order (MP4SDQ including only single, double, and quadruple electron excitations; triple substitutions have been neglected) using HF wave functions computed at HF/6-31G**-optimized geometries with the 6-31G** basis set for generating electronic configurations. All calculations were performed employing a local version of the Gaussian-82 program[17] that includes, among other things, the Hessian mode-following algorithm for locating transition structures.[18] Unless otherwise noted, our relative energies mentioned hereafter are obtained from MP4SDQ/6-31G** energies corrected for zero-point contributions. Throughout this paper, bond lengths are given in angstroms and bond angles in degrees. The dipole moments are obtained from HF/6-31G** wave functions.

Scheme I

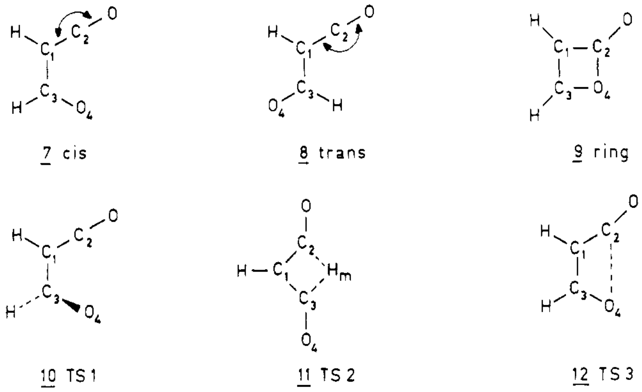


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Table II. Calculated Total (Hartrees), Zero-Point Vibrational (kcal/mol), and Relative (kcal/mol) Energies for Points on the Formylketene Potential Energy Surface Using the 6-31G Basis Set**

level[a]	7 (cis)	8 (trans)	9 (ring)	10 (TS1)	11 (TS2)	12 (TS3)
			Total Energies			
HF	-264.461 03	-264.459 60	-264.427 24	-264.440 96	-264.373 11	-264.415 40
MP2	-265.187 81	-265.187 07	-265.159 10	-265.167 88	-265.127 25	-265.157 02
MP3	-265.190 00	-265.189 47	-265.165 34	-265.172 22	-265.117 79	-265.154 35
MP4 (SDQ)	-265.207 13	-265.206 41	-265.179 30	-265.189 23	-265.138 33	-265.172 45
ZPE[b]	26.7	26.4	26.7	25.8	23.2	25.9
			Relative Energies			
HF	0.0	0.9	21.2	12.6	55.2	28.6
MP2	0.0	0.5	18.0	12.5	38.0	19.3
MP3	0.0	0.3	15.5	11.2	45.3	22.4
MP4 (SDQ)	0.0	0.5	17.5	11.2	43.2	21.8
MP4 + ZPE[c]	0.0	0.2	17.5	10.3	39.7	21.0

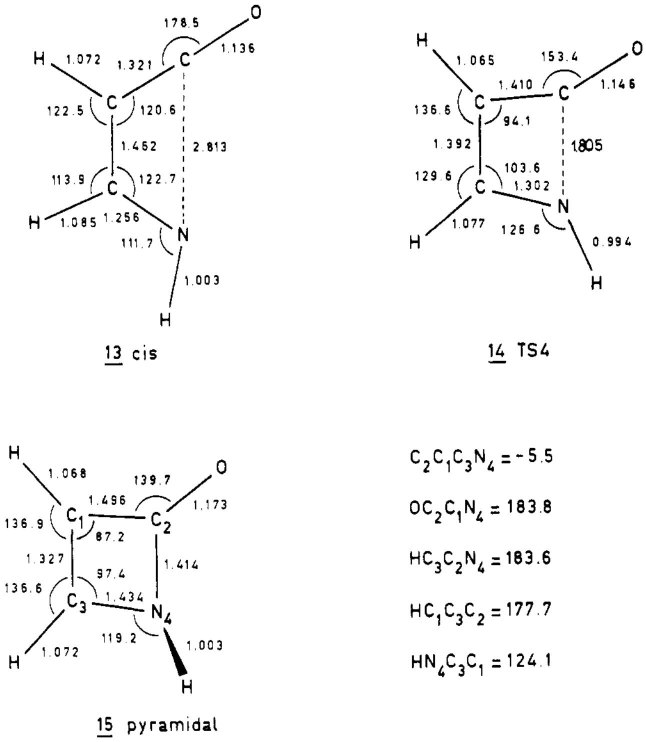
[a] Using HF/6-31G**-optimized geometries given in Table I. [b] Zero-point energies computed at HF/3-21G and scaled by 0.9. [c] Including MP4SDQ values and zero-point energies.

3. Results and Discussion

3.1. Rearrangement and Ring-Closure of Formylketene.

The six stationary points involved in the unimolecular rearrangement and ring-closure of the formylketene molecule are shown in Scheme I. They include both the cis 7 and trans 8 forms of formylketene, the oxetone ring 9, and three transition structures, namely, the TS1 10 for cis–trans isomerization, the TS2 11 for 1,3-hydrogen shift, and the TS3 12 for ring-closure. Their geometrical parameters optimized using the HF/6-31G** model are listed in Table I, while the corresponding total and relative energies are recorded in Table II.

The C1–C3 distances in both isomers 7 and 8 (1.460–1.463 Å) are similar to that of 1.478 Å in *trans*-acrolein and that of 1.467 Å in *trans*-butadiene (values at HF/6-31G**). Compared with the values calculated for the unsubstituted ketene ($H_2C{=}C{=}C$: C=C, 1.306 Å; C=O, 1.145 Å with HF/6-31G**), the C1–C2 bond lengths in 7 and 8 are slightly stretched, while the C2–O distances are somewhat compressed. However, the sum of both distances remains almost unchanged upon substitution. At the level of theory employed here, the cis form 7 is calculated to lie marginally lower in energy than the trans 8 by 0.2 kcal/mol. The cis isomer 7 has also a larger dipole moment (3.6 D) than the trans 8 (2.4 D). The two forms are connected by the transition structure for rotation, TS1 9. The corresponding rotational barrier amounts to 10.3 kcal/mol. We note that the barrier height of 11.7 kcal/mol at the HF/6-31G** + ZPE level is, for example, somewhat higher than the relevant value of 8 kcal/mol found in the acrolein molecule. Thus, a significant amount of the trans form should exist in equilibrium with the more stable cis form. On the other hand, bulky substituents may also favor the trans isomer, which has the right nuclear configuration for the carbon scrambling of a substituent.[12] In the simplest case considered here involving migration of the hydrogen from carbon to carbon in formylketene, a rather substantial energy barrier has been calculated. For instance, the barrier height of 39.5 kcal/mol via the transition structure TS2 11 (cf. Table II) is even larger than that of 33 kcal/mol previously computed for the 1,3-hydrogen shift in formic acid[19] (at a similar level). This indicates that the phenyl shift in acetylketene observed by Wentrup and Netsch[12] is due to the larger migratory aptitude of that group. Nevertheless, these authors[12] also pointed out a significant activation energy for the phenyl migration (no scrambling was observed at temperature of 400 °C). Appropriate calculations on the 1,3-shift of the phenyl group are no doubt necessary for a quantitative comparison, but here we wish to note that the keto-ketene–ketoketene rearrangement involving a hydrogen migration remains a rather difficult chemical process.



13 cis

14 TS4

$C_2C_1C_3N_4 = -5.5$

$OC_2C_1N_4 = 183.8$

$HC_3C_2N_4 = 183.6$

$HC_1C_3C_2 = 177.7$

$HN_4C_3C_1 = 124.1$

15 pyramidal

Figure 1. HF/6-31G**-optimized geometries for points on the imidoylketene energy surface.

As seen in Table II, at all levels of theory considered, the cyclic oxetone 9 is computed to be higher in energy than *cis*-formylketene 7. As usual, electron correlation tends to reduce the energy difference between them. The cyclization of formylketene 7 takes place through the transition structure TS3 12. At this point, the C2–O4 distance, which can be considered as the reaction coordinate, reaches the value of 1.756 Å, which is rather close to that in the ring 9 (1.413 Å). Our best estimates predict that the *cis*-formylketene 7 lies 17.5 kcal/mol below its cyclic isomer 9 and undergoes ring-closure with an energy barrier of 21.0 kcal/mol. Proceeding in the opposite direction, the four-membered ring 9 is found to rearrange to its open-chain isomer 7 with a barrier of only 3.5

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Table III. Calculated Total (Hartrees), Zero-Point Vibrational (kcal/mol), and Relative (kcal/mol) Energies for Points on the Imidoylketene Potential Energy Surface Using the 6-31G Basis Set**

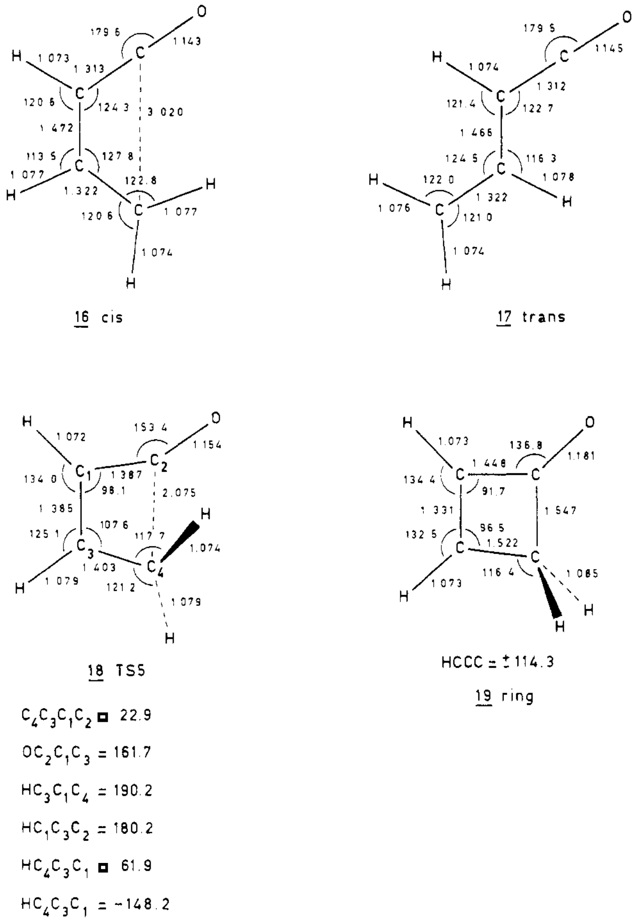
level[a]	13 (cis)	13 (trans)	14 (TS4)	15 (pyramidal)	15 (planar)
			Total Energies		
HF	-244.618 70	-244.618 20	-244.570 59	-244.599 56	-244.591 15
MP2	-245.338 27	-245.338 15	-245.302 39	-245.322 32	-245.312 52
MP3	-245.349 86	-245.350 14	-245.308 26	-245.336 02	-245.326 12
MP4 (SDQ)	-245.363 69	-245.363 75	-235.322 92	-245.347 73	-245.337 98
ZPE[b]	34.1	33.8	32.9	34.0	33.7
			Relative Energies		
HF	0.0	0.3	30.1	12.0	17.3
MP2	0.0	0.1	22.5	10.0	16.2
MP3	0.0	-0.2	26.1	8.7	14.9
MP4 (SDQ)	0.0	-0.04	25.6	10.0	16.1
MP4 + ZPE[c]	0.0	-0.3	24.4	9.9	15.7

[a] Using HF/6-31G**-optimized geometries given in Figure 1 for structures **13** (cis), **14** (TS4), and **15** (pyramidal). [b] Zero-point energies computed at HF/3-21G and scaled by 0.9. [c] Including MP4SDQ values and corrected for zero-point contributions.

kcal/mol. Accordingly, the oxetone **9** can hardly be stable, even in the gas phase, as a discrete species. This result is in agreement with experimental observation showing that acylketenes do not cyclize but instead dimerize.[11]

3.2. Ring-Closure of Imidoylketene. The optimized structures for the three stationary points of interest on the imidoylketene potential energy surface are displayed in Figure 1. The imidoylketene molecule can exist in four different conformations and configurations. To simplify the presentation of data, we show in Figure 1 only the cis form **13** which has the appropriate nuclear disposition for undergoing cyclization.

However, for the sake of comparison, energetics of the corresponding trans form are also included in Table III. In the same manner, the geometry of the planar cyclic azetinone **15** is not shown, but its energies are included in Table III. The cis form of imidoylketene is calculated to be more stable than the trans form by 0.3 kcal/mol. The former has, however, a larger dipole moment (3.2 D) than the latter (1.2 D). The four-membered ring azetone **15** possesses, for its part, a pyramidal structure at nitrogen. The planar structure is characterized as a transition structure for nitrogen inversion. The corresponding barrier to inversion amounts to 5.8 kcal/mol (cf. Table III) which is of the same order of magnitude as that in ammonia. Previously, Olofson and co-workers[8] have reported the crystal structure of the *N*-adamantylbenzoazetinone. We note initially that the C1–C3 distance is significantly longer in the benzo-fused form (1.388 and 1.411 Å, respectively, instead of 1.327 Å in structure **15**). More importantly, the crystal structure reveals a flat configuration with a sp_2 hybridization at the nitrogen center. Such an unusual feature, which apparently violates the classical Hückel's rule, by implying a contribution of antiaromatic amide resonance, may thus arise from a peculiar effect of the electron delocalization in the fused form. Further calculations are needed to clarify this interesting structural behavior of the benzoazetinone molecule. Our calculated energy difference between the open-chain cis **13** and ring pyramidal **15** is 9.9 kcal/mol in favor of the open form. The latter undergoes 1,4-electrocyclization via the transition structure TS4 **14** with an energy barrier of 24.4 kcal/mol. Proceeding in the opposite direction, the ring-opening of azetone **15** needs to surmount a smaller energy barrier of 14.5 kcal/mol (cf. Table III). Recent MNDO calculations[9] on the reaction pathway **13** → **14** → **15** predicted, among other things, a comparable energy pattern; namely, the reaction enthalpy ($\Delta H_r°$) for the cycloreversion **15** → **13** is 9.9 kcal/mol, and the corresponding activation enthalpy ($\Delta H^‡$) is 11.6 kcal/mol. Thus the semiempirical MNDO method reproduces relatively well the ring–chain energy difference but underestimates the activation energy. An analysis of substituent effects on the equilibrium **15** → **13** is also available.[9]



16 cis

17 trans

18 TS5

19 ring

Figure 2. HF/6-31G**-optimized geometries for points on the vinylketene energy surface.

At this stage of our study, it can be concluded that, in the gas phase, the nonfused azetinone rings should be too unstable both thermodynamically and kinetically with respect to their more stable open-chain isomers. However, an energy barrier of 14.5 kcal/mol appears to be large enough to allow the heterocyclic species to be formed, for example, in an inert matrix at low temperature, or as a reactive intermediate at higher temperature in solution.

3.3. Ring-Closure of Vinylketene. The optimized structures for the vinylketene systems are shown in Figure

Table IV. Calculated Total (Hartrees), Zero-Point Vibrational (kcal/mol), and Relative (kcal/mol) Energies for Points on the Vinylketene Potential Energy Surface Using the 6-31G Basis Set**

level[a]	**16** (cis)	**17** (trans)	**18** (TS5)	**19** (ring)
		Total Energies		
HF	-228.611 65	-228.614 43	-228.548 19	-228.611 01
MP2	-229.306 34	-229.308 88	-229.262 92	-229.307 91
MP3	-229.325 40	-229.328 20	-229.275 28	-229.328 80
MP4 (SDQ)	-229.338 55	-229.341 19	-229.287 66	-229.339 81
ZPE[b]	40.6	40.7	39.8	41.4
		Relative Energies		
HF	0.0	-1.7	39.8	0.4
MP2	0.0	-1.6	27.2	-1.0
MP3	0.0	-1.8	31.5	-2.1
MP4 (SDQ)	0.0	-1.7	31.9	-0.8
MP4 + ZPE[c]	0.0	-1.6	31.1	0.0

[a] Using HF/6-31G**-optimized geometries given in Figure 2. [b] Zero-point energies computed at HF/3-21G and scaled by 0.9. [c] Including MP4SDQ values and corrected for ZPE corrections.

2 while the relevant energetics are listed in Table IV. Vinylketene itself was generated mostly in the gas phase[20] and has been well-characterized by different spectroscopic techniques which include the microwave,[21] photoelectron,[22] mass,[23] and infrared[24] spectroscopies. This molecule has also attracted interest as a member of the interstellar series of high-carbon-containing chain H_4C_nO molecules.

The microwave experiment[21] revealed that vinylketene exists in the gas phase in its trans form. Attempts to find spectral lines from the cis isomer were unsuccessful. Our calculations concur with this. We find that the cis form **16** is a local minimum on the potential energy surface and lies only 1.6 kcal/mol above the trans **17** (cf. Table IV). However, separate calculations at the HF level indicate that the rotation around the C1–C3 bond of vinylketene is an easy process with a rotational barrier of only 2–3 kcal/mol from the cis isomer **16**. In this context, the *cis*-vinylketene **16** can hardly be detectable in the flash photolysis experiment at high temperature (500 °C).[21] For substituted vinylketenes, a ratio trans:cis of about 6:4 has been found under various thermal and photochemical conditions.[25] This is in line with the small isomerization energy mentioned above.

At the HF/6-31G** level, the dipole moments are calculated to be 1.6 ad 1.2 D for the cis **16** and trans **17**, respectively. The latter value compares favorably with the microwave estimate of 0.97 D.[21] We note that the dipole moment of the ketene series actually decreases in the sequence, formyl (3.6 D) > iminoyl (3.2 D) > vinyl (1.6 D) (values for the cis isomers). The low magnitude in the vinyl member has been rationalized in terms of a larger π-electron delocalization of the oxygen lone pair onto the C=C moiety which reduces consequently the $>C^+—C=O^-$ polarity.[21] The reorganization of the charge distribution in the four-membered ring **19** results in a rather large dipole moment of 3.7 D as compared with its open-chain isomer (see above). The dipole moment of the transition state TS5 **18** is also large (2.9 D). Not surprisingly, first-order rate constants for the conversion of cyclobutenones into vinylketenes have been found to be inversely dependent on solvent polarity.[3] As a matter of fact, solvents with large polarity should favor the formation of the cyclic form and slow down the ring-opening process.

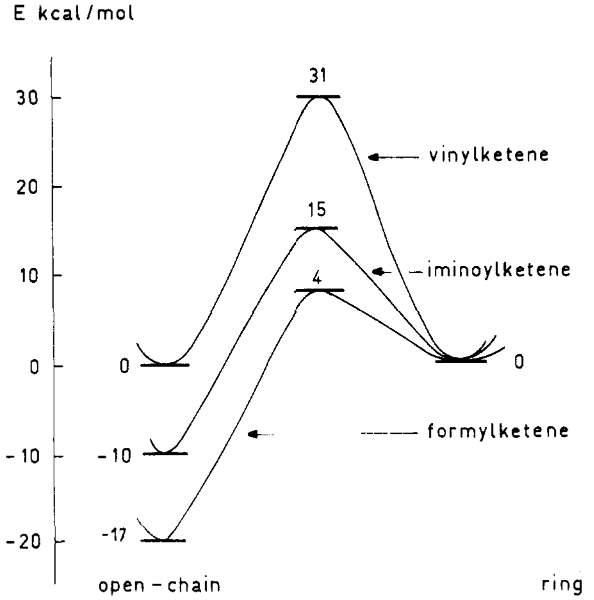


Figure 3. Schematic energy profiles for the ring–chain isomerizations in the vinyl-, imidoyl-, and formylketene systems.

At the level of theory employed in the present work, the *cis*-vinylketene **16** and cyclobutenone **19** isomers are calculated to be almost isoenergetic. Their interconversion occurs through the transition structure TS5 **18** and encounters a more substantial energy barrier of 31.1 kcal/mol (cf. Table IV). This result is consistent with the experimental observation of both forms which exist in equilibrium.

4. Comparison and Summary

The energy profiles of the three ring-chain isomerization are shown schematically in Figure 3. The endothermicity of the ring-closure reaction is reduced in the sequence formylketene → imidoylketene → vinylketene. Thus, the successive replacement of O by NH, and NH by CH_2, destabilizes the open-chain form (or conversely stabilizes the cyclic form) with respect to its isomer by an energy of about 10 kcal/mol. Conversely, the activation barrier for ring-opening decreases more rapidly in going from cyclobutenone to azetinone (16 kcal/mol) than from azetinone to oxetone (11 kcal/mol). Within the framework of the Marcus theory,[26] the thermoneutrality of the vinylketene ring–chain tautomerism provides us with a change to obtain the "intrinsic barrier" $\Delta G_0^\ddagger$. Employing the calculated entropy variation $\Delta S^\ddagger = 3$ cal/mol·K, the intrinsic barrier for the cyclization is calculated as $\Delta G_0^\ddagger = 30$ kcal/mol at 300 K. Nevertheless, we note that the free energy of activation ($\Delta G^\ddagger$) predicted for the formylketene and iminoylketene systems employing the relationship:

$$\Delta G^\ddagger = \Delta G_0^\ddagger(1 + \Delta G/4\Delta G_0^\ddagger)^2$$

and the relevant $\Delta G^\ddagger$ values deviate significantly from the directly computed values discussed above. This indicates that the three cyclizations being considered do not belong

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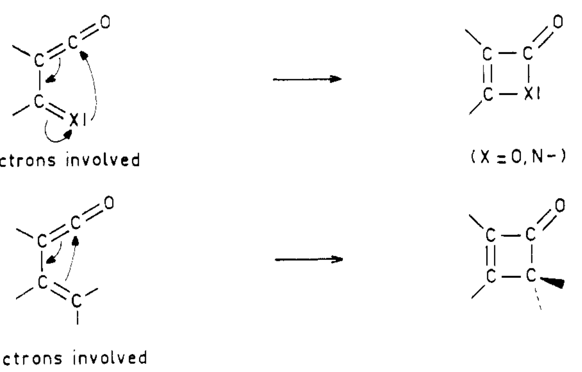
Scheme II



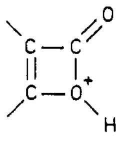
to a homogeneous series. With regard to the four-membered rings, antiaromaticity may partly account for the change in the endothermicity. Replacing O by CH_2 removes any antiaromatic character (4 π-electrons) of the ring and thus increases its stability. It is worth noting the energy difference between the four-membered cycles and the corresponding fragments (values given in kcal/mol at the MP4/6-31G** + ZPE level):

$$\mathbf{9} \rightarrow O{=}C{=}O + HC{\equiv}CH \quad \Delta E = -10.0$$

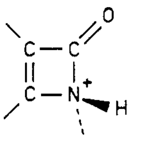
$$\mathbf{15} \rightarrow HN{=}C{=}O + HC{\equiv}CH \quad \Delta E = 11.0$$

$$\mathbf{19} \rightarrow H_2C{=}C{=}O + HC{\equiv}CH \quad \Delta E = 40.0$$

Thus, oxetone is also unstable with respect to the [2 + 2] cycloreversion process. In this context, it is interesting to speculate that the protonated forms of oxetones **20** and azetinones **21** might have a greater stability with respect to ring-opening than the neutral species. By the same token, the neutral species may show an enhanced stability which, if the azetinone could be generated in acidic media, might be revealed by an equilibrium or kinetic pK_a measurement.

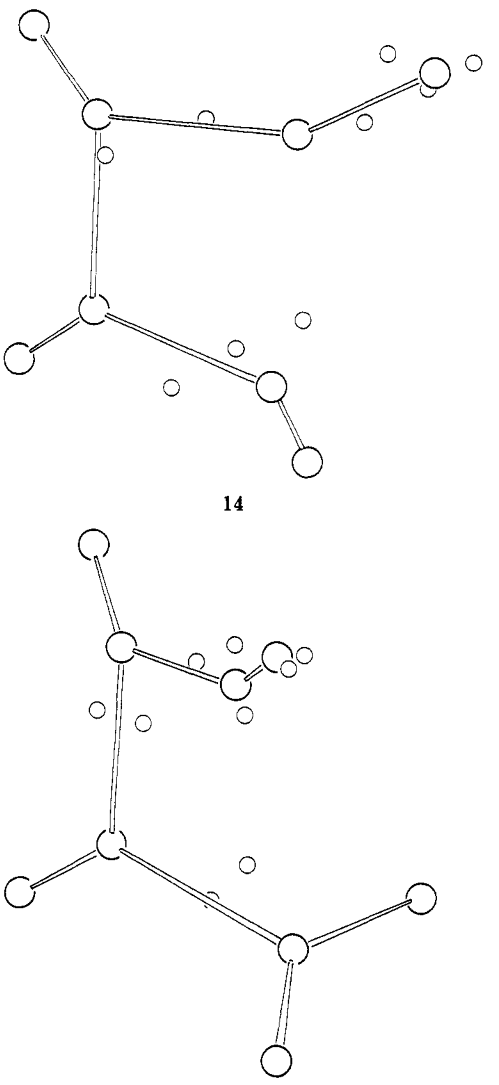


20



21

It is also interesting that in **21** protonation is implied at the nitrogen atom rather than the normal carbonyl site of simple amides. We now compare the electrocyclic ring-opening reactions being examined with that of cyclobutene to butadiene. The transition structure and activation barrier for this reaction have been studied extensively in the past.[27] Geometrical parameters of the transition structure are reasonably insensitive to changes in the basis sets or inclusion of electron correlation. At the MP2/6-31G**//MP2/6-31G* level, for example, the barrier height for ring-opening of cyclobutene amounts to 36.8 kcal/mol which is somewhat larger than the experimental value of 34.5 kcal/mol[27] (values without zero-point corrections). We also note that the triple substitutions in the perturbation expansion reduce the barrier height by 3 kcal/mol. Hence, our estimates obtained from the MP4SDQ/6-31G** level are probably overestimated by 2–3 kcal/mol. As shown in ref 27, the MP2/6-31G** values may paradoxically lie closer to the true ones. In summary, the electrocyclic ring-opening of cyclobutenone is energetically more favorable than that of cyclobutene by ca. 6–8 kcal/mol with regard to the barrier height.



14

18

Figure 4. Centroids of charge of the localized molecular orbitals (LMO) in the transition structures **14** and **18** for the ring-opening of azetone and cyclobutenone, respectively (at HF/6-31G**).

Finally, an analysis of the localized orbital[28] of the points on the reaction pathways allows us to show the electronic reorganization occurring (cf. Figure 4). Scheme II summarizes the main features of the electronic mechanism of the ring-closure of substituted ketenes. The difference between vinylketene and others relates to the nature of electron pairs involved in the cyclic migration. This movement depends on whether or not the center X (Scheme II) can donate or accept a lone pair. In this regard, the ring-closure is quite similar to that of vinylazide and imidoylazide.[29]

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