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Facile 1,3-Shift of Chlorine in a Chlorocarbonylketene

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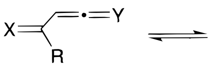
Abstract: Chlorocarbonyl(phenyl)ketene (**2**) undergoes a degenerate 1,3-shift of chlorine, as determined by ^{13}C NMR spectroscopy. The two carbonyl signals (183 and 157 ppm) coalesce at −30 °C, and from this as well as line-shape analysis, an activation barrier for the 1,3-Cl shift interconverting **2a** and **2a′** of $\Delta G^{\ddagger} = 41.8 \pm 4$ kJ mol^{-1} (10.0 ± 1 kcal mol^{-1}) is calculated. These data are in excellent agreement with calculated (G2(MP2,SVP) and B3-LYP/6311+G(3df,2p)//6-31G* + ZPVE) 1,3-Cl shift and rotational barriers. Analogous 1,3-halogen shifts in acyl isocyanates are predicted.

Introduction

In previous work from this laboratory it was demonstrated that α-oxo ketenes **1a** can undergo degenerate 1,3-shifts of the substituents R under the conditions of flash vacuum thermolysis (FVT).[2]



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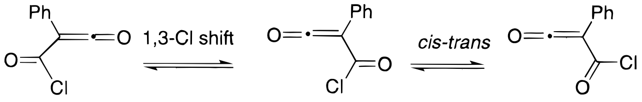
a: X = O, Y = O
b: X = NR', Y = O
c: X = CR'$_2$, Y = O

Experiments on the related imidoylketene−α-oxo ketenimine (**1b**/**1′b**)[3] and vinylketene−acylallene (**1c**/**1′c**) rearrangements[4] as well as ab initio calculations[5] on the α-oxo ketenes revealed an accelerating effect of electron-rich substituents, e.g., MeO, MeS, and Me$_2$N, which was ascribed to a favorable interaction between a lone pair located on the substituent and the low-lying ketene LUMO, which has a large coefficient at the central ketene carbon atom. The same effect was also predicted for chlorine, with a calculated 1,3-shift barrier of 53 kJ mol^{-1}.[6] In other words, we should expect such 1,3-shifts of chlorine (and other lone-pair donors such as NMe$_2$) to take place at temperatures well below ambient. However, all our previous experiments have been performed in the gas phase under FVT conditions, and the lowest temperature where such observations were practicable were ∼200 °C (for MeO and MeS groups).[3,4] This temperature was not necessarily limited by the activation barrier for the 1,3-shift, but rather by the barriers required to generate the ketenes or ketenimines from the requisite precursors. Taking advantage of the fact that chlorocarbonyl(phenyl)ketene (**2**) is an isolable compound,[7] we have carried out a variable-temperature ^{13}C NMR investigation of this compound and report direct experimental proof of the rapid 1,3-chlorine shift, taking place at −30 °C with a barrier of ∼42 kJ mol^{-1}.

Results and Discussion

The ^{13}C NMR spectrum of **2** features a single, slightly broadened signal in the carbonyl region at 171 ppm at room temperature (Figure 1a). At higher temperatures, this signal sharpens, but otherwise the spectrum remains unchanged up to ∼150 °C, when the compound starts decomposing (in nitrobenzene-d_5 solution). In contrast, cooling the solution (in CD$_2$Cl$_2$) causes the carbonyl signal to all but vanish near −30 °C, with formation of a very broad, flat-topped coalescence peak spanning a range of some 40 ppm (Figure 1b). At −40 °C there is already decoalescence, and at −60 °C two well-defined carbonyl signals appear at 183 and 157 ppm (Figure 1c). From the coalescence temperature (T_c) of −30 °C, a free energy of activation $\Delta G^{\ddagger} = 41.6$ kJ/mol is calculated.[8] Line-shape analysis[8a,b] of these signals from +35 to −60 °C afforded $\Delta G^{\ddagger} = 41.8$ kJ/mol and $T_c = -29$ °C.



2a 2a' 2b

The aromatic carbon signals of **2** appeared at 124.5 (*ipso*-C), 128.8, 128.7, and 129.7 ppm (0 °C). This region of the ^{13}C NMR spectrum remained unchanged at −60 °C. The terminal ketene ^{13}C signal remained constant and sharp at 63.5

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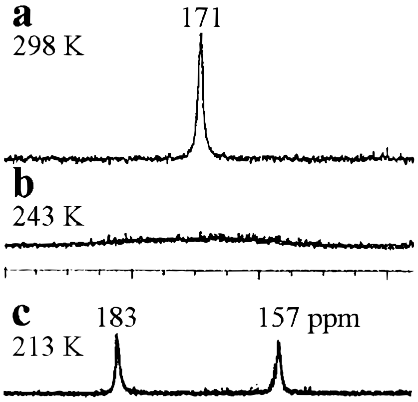

Figure 1. ^{13}C NMR spectra of the carbonyl group region of 2 at various temperatures: (a) 25 °C, (b) −30 °C; the divisions are 5 ppm; and (c) −60 °C.

ppm throughout the temperature range. The downfield shift observed for all ^{13}C NMR signals at lower temperatures is a common occurrence.

Values for $\Delta G^{\ddagger}$(cis−trans) will be the subject of future studies of other ketenes. However, a rotational barrier of ~48 kJ mol^{-1} (see below) is perfectly reasonable and comparable with those in diazocarbonyl compounds (38−75 kJ mol^{-1}).[9] The fact that the ^{13}C NMR peaks for the aryl carbons and for the terminal ketene carbon atom remained unsplit means either that the chemical shift differences between these signals in **2a** and **2b** are too small to cause resolution at the temperatures reached here or that only **2a** is present, in agreement with the calculations below.

Theory

We have previously reported the effect of substituents on the 1,3-migration in α-oxo ketenes at the QCISD(T)/6-311+G(2d,p)//MP2/6-31G* + ZPVE level.[5] Here, we have calculated the 1,3-shift barriers at a higher level of theory, G2(MP2,SVP),[10,11] and extended the list of substituents (Table 1). It is seen that substituents with unshared pairs of electrons are good migrators, which is understood in terms of the favorable interaction between the lone pair of the migrating atom and the vacant central carbon p orbital of the ketene LUMO.[4,5] Thus, the dimethylamino group is predicted to be the best migrator with a 1,3-shift barrier of only 34 kJ mol^{-1}. Indirect evidence for rapid 1,3-shifts of the dimethylamino group in dimethylamidoketenimines (**1′**b, R = NMe$_2$) below room temperature will be published elsewhere.[12] 1,3-Migrations involving PH$_2$, SH, SCH$_3$, Cl, and Br can also be expected to be very facile processes, of which only the SMe shift has been observed so far, and then only in the gas phase above 200 °C.[3] The calculated barriers for the 1,3-halogen shifts follow the order expected from the relative nucleophilicities. In addition, the four-membered ring transition structures containing Cl or Br may be significantly less strained as judged from the larger calculated CCC bond angles (105, 111, and 114° for R = F, Cl, and Br, respectively).

Table 1. Calculated Relative Energies (kJ mol^{-1}) of α-Oxo Ketenes (RC(=O)CH=C=O)[a]

R	s-trans	s-cis	1,3-shift barrier
CH$_3$	0.0	0.3	206.0
H	0.0	1.8	142.7
SiH$_3$	0.0	0.0	119.7
OH	0.0	1.8	114.5
OCH$_3$	0.0	1.8	97.9
F	0.0	2.2	88.8
NH$_2$	0.0	−5.2	69.6
PH$_2$	0.0	−1.3	58.9
Cl	0.0	4.2	52.7
SH	0.0	−2.7	51.5
SCH$_3$	0.0	−3.3	47.2
Br	0.0	4.2	38.9
N(CH$_3$)$_2$	0.0	−7.2	33.9

[a] G2(MP2,SVP) values.

Since it is not feasible to perform G2(MP2,SVP) calculations for chlorocarbonyl(phenyl)ketenes (**2a** and **2b**), we have examined the energies of this system, using a density functional method, at the B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G* + ZPVE level.[14] At this level of theory, the calculated 1,3-H shift barrier of the parent formylketene (**1a**, R = H) is 139 kJ mol^{-1}, in good agreement with the G2(MP2,SVP) value (143 kJ mol^{-1}). The rotational barriers are virtually identical at the B3-LYP and G2(MP2) levels. This lends confidence to the B3-LYP barriers for **2**. The calculated 1,3-Cl shift barrier in **2** is 36 kJ mol^{-1}, and for chloroformylketene (**1a**, R = Cl) it is 53 kJ mol^{-1}. The lowering by 17 kJ mol^{-1} may be understood in terms of extra stabilization of the planar transition structure (Figure 2) due to conjugation with the phenyl ring. Both the s-trans (**2a**) and the s-cis conformation (**2b**) are significantly distorted from planarity. The dihedral angles between the phenyl group and the ketene moiety are 37° and 67° in **2a** and **2b**, respectively (Figure 2). The s-cis rotamer (**2b**) is computed to be 10 kJ mol^{-1} less stable than the s-trans form. The calculated cis−trans isomerization barrier is 48 kJ mol^{-1}, and the barrier for rotation of the phenyl group in the s-trans form (**2a**), via a planar transition structure, is ~3 kJ mol^{-1}. The reason for this exceptionally low barrier may be found in the stabilization of the planar transition structure due to conjugation.

In previous computational work we found that different substituents may stabilize either the s-cis or the s-trans form of acylketenes, acylketenimines, imidoylketenes, and vinylketenes within a ~10 kJ mol^{-1} range.[4−6]

The calculated ΔE, ΔH, ΔS, and ΔG values for chlorocarbonyl(phenyl)ketene are summarized in Table 2. The entropy values and temperature corrections ($H_T - H_0$) were derived from B3LYP/6-31G* frequency calculations. The enthalpies of reaction (ΔH) were obtained by adding the thermal correction to ΔE, and the final ΔG values were computed from the equation $\Delta G = \Delta H - T\Delta S$. Since the B3-LYP barrier is slightly underestimated by ~4 kJ mol^{-1}(vide supra), our best estimate of $\Delta G^{\ddagger}$ for the 1,3-Cl shift is 39 kJ mol^{-1}, in excellent agreement with the experimental value (42 kJ mol^{-1}).

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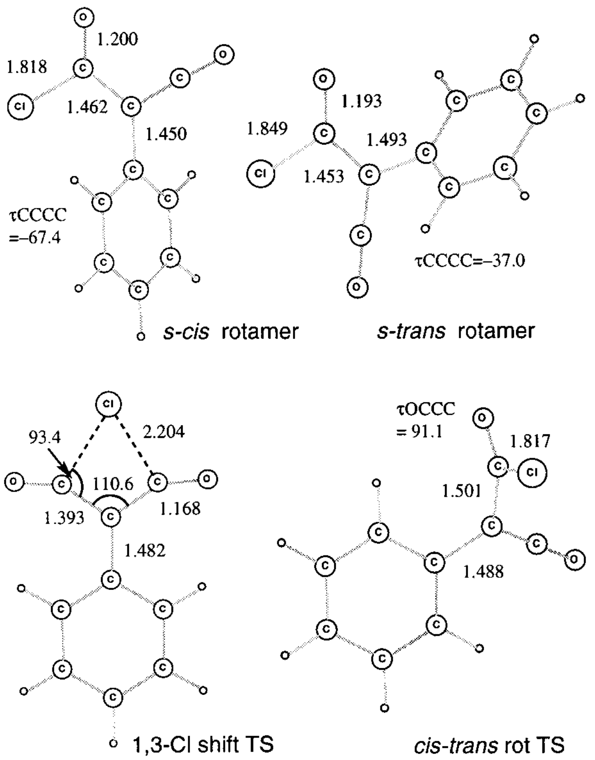


Figure 2. B3-LYP/6-31G* calculated structures of s-cis (**2b**) and s-trans (**2a**) chlorocarbonyl(phenyl)ketene, and the transition structures for the 1,3-chlorine shift and for cis−trans isomerization in **2**. Bond lengths are in angstroms, and angles, in degrees.

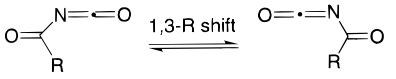
Table 2. Calculated Energies of Chlorocarbonyl(phenyl)Ketene **2**[a]

species	ΔE (0 K)[b]	ΔH −30 °C	25 °C	ΔS	ΔG −30 °C	25 °C
s-trans (**2a**)	0.0	0.0	0.0	0.00	0.0	0.0
s-cis (**2b**)	10.1	10.2	10.3	1.23	10.0	10.0
1,3-Cl shift TS	35.9	34.8	34.3	−2.60	35.5	35.1
cis−trans rot. TS	47.7	46.3	45.5	−3.31	47.1	46.5
phenyl rot. TS (in s-trans **2a**)	2.8	0.7	1.5	−6.42	2.3	3.4

[a] In kJ mol^{-1}, except for ΔS in J mol^{-1} K^{-1}. [b] B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G* + ZPVE.

Acyl Isocyanates

The degenerate 1,3-shifts observed in α-oxo ketenes may also be expected in acyl isocyanates **3**, but the calculated activation barriers are higher: H (207), F (116), Cl (84.5), and Br (72 kJ mol^{-1}) at the G2(MP2,SVP) level. From the measured ^{13}C



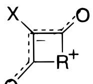
3 **a**: R = F
b: R = Cl
c: R = Br

NMR spectrum[15] of **3b** and the calculated $\Delta G^{\ddagger} = 84.5$ kJ mol^{-1}, one estimates[8a] a coalescence temperature T_c of 188 °C at 100.4 MHz. The high T_c is due to the large $\Delta\nu$ for the two carbonyl signals for this compound (1131 Hz in a field of 100.4 MHz). The low boiling point of this compound (63 °C) unfortunately puts this experiment outside the range accessible by liquid-phase ^{13}C NMR spectroscopy, even though the rearrangement is in fact expected to take place at room temperature. Our ^{13}C NMR measurements for this compound at temperatures up to the boiling point showed two carbonyl signals (δ 141.0 and 129.8 in CDCl$_3$) and no sign of line broadening. For the analogous fluoro compound **3a**, one calculates in the same manner T_c = 344 °C at 100.4 MHz; the observation of this 1,3-shift by ^{13}C NMR spectroscopy is out of the question, although the reaction should take place not far above room temperature. It remains uncertain whether the reported broadness[16] of the ^{19}F NMR signal for this compound is due to such fluorine migration. However, the bromide **3c** is a candidate for experimental observation of a 1,3-Br shift at a calculated T_c of ~150 °C.

As in the case of the imidoylketenes and vinylketenes,[4] the higher barriers in the acyl isocyanates relative to α-oxo ketenes can be explained by the energy of the acceptor orbital (the LUMO of the cumulene). For instance, the LUMO energies (HF/6-31G*) calculated for formylketene and formyl isocyanate are 2.54 and 2.77 eV, respectively.

Conclusion

We have experimentally verified a remarkable theoretical prediction, viz. the degenerate 1,3-Cl shift in chlorocarbonylketene **2**, with an activation barrier of ~42 kJ mol^{-1} (10 kcal mol^{-1}). Other facile 1,3-shifts of this type, e.g., of Br, SMe, NMe$_2$, PR$_2$, F, and OR groups are to be expected, and such reactions are the subject of ongoing research in our laboratories. The question of stabilizing four-membered ring zwitterionic transition states or intermediates of the type **4** in such reactions is under continuing investigation.



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Experimental Section

Chlorocarbonyl(phenyl)ketene (2). The literature procedure[7a] gave various mixtures of the desired ketene **2** and phenylmalonyl dichloride. Procedures using PCl$_5$[7b−d] were found to be undesirable as significant decomposition occurred. The following procedure gave reproducible results. A mixture of 50 g (0.28 mol) of phenylmalonic acid and 250 mL of freshly distilled thionyl chloride in a 500-mL three-necked round-bottomed flask equipped with a condenser and a CaCl$_2$ drying tube was refluxed at 85−95 °C for 48 h. A second batch starting from 25 g (0.14 mol) of phenylmalonic acid was prepared analogously. After the two batches were combined and excess thionyl chloride distilled, the resultant oil (60 g) was found by ^{1}H and ^{13}C NMR (vide infra) to be a mixture of ketene **2** (50−70%) and phenylmalonyl dichloride (50−30%). This crude mixture was refluxed without solvent for 5 h at 2 mbar using a KOH trap and a liquid N$_2$ trap in series to collect the evolved HCl. The resulting oil was purified by repeated distillation (first at 80−94 °C/2 mbar, then at 82−86 °C/2 mbar) using a 25 cm Vigreux column to give 56 g (74%) of ketene **2** as an orange oil. NMR analysis of different batches demonstrated that the ketene was of 95−98% purity, the remaining 5−2% being phenylmalonyl dichloride.

A sample of phenylmalonyl dichloride was prepared for comparison using the method of Stensrud et al.[17a] This procedure yields a mixture

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consisting of ~82% of the dichloride and 18% of ketene **2**. Thealternative procedure of Sorm et al.[17b] using PCl_5 is undesirable because of low yields and much decomposition.

^{1}H NMR ($CDCl_3$, 200 MHz): (phenylmalonyl dichloride) δ 5.40 (s, 1H), 7.35−7.48 (m, 5H); (ketene **2**): δ 7.25−7.46 (m). ^{13}C NMR ($CDCl_3$, 50 Hz) (phenylmalonyl dichloride): δ 76.8, 128.3, 129.5, 129.6, 130.2, 166.4; (ketene **2** (0 °C)): 63.5 (*C*═C═O), 124.5 (*ipso*-C), 128.7, 128.8, 129.7 (arom.), 170.3 (C═*C*═O). IR (film): ν 2128 cm^{-1}.

Variable-temperature NMR spectroscopy was performed on a JEOL EX-400 spectrometer (100.5 MHz for carbon). The temperatures were calibrated using the ^{1}H NMR chemical shift difference of the signal of neat MeOH (low-temperature region) or 1,3-propanediol (high-temperature region). CD_2Cl_2 and nitrobenzene-d_5 were used as solvents for low and high temperatures, respectively. Solutions of **2** (200−250 mg) in 0.5−0.6 mL of the solvent were sealed in NMR tubes under N_2. Spectra were recorded between −60 and +180 °C.

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Supporting Information Available: Calculated E_0 energies (G2(MP2,SVP)) of α-oxo ketenes and acyl isocyanates (in hartrees); calculated total energies, ZPVEs, temperature corrections, and entropies of **2a** and **2b**; optimized B3-LYP/6-31G* equilibrium and transition structures of **2** in Cartesian coordinates, and energy profile for rotation of the phenyl ring in the s-trans **2a** (5 pages). See any current masthead page for ordering information and Web access instructions.

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