PERKIN 2

The thioacyl isocyanate–acyl isothiocyanate rearrangement†

Rainer Koch*[a] **and Curt Wentrup***[b]

[a] *Fachbereich Chemie der Carl von Ossietzky Universität Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany*
[b] *Department of Chemistry, The University of Queensland, Brisbane, Qld. 4072, Australia*

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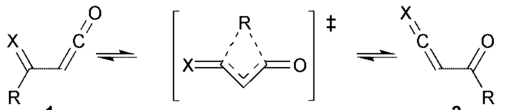
The title rearrangement, involving a 1,3-shift of a substituent on an acyl(thioacyl) group is investigated computationally at *ab initio* and DFT levels of theory (G2(MP2,SVP) and B3LYP/6-31G*). The computed order of migratory aptitudes is Br > Cl > NMe_2 > F, SCH_3, SH > OMe, NH_2 > OH ⩾ H ⩾ Me, in good agreement with experimental data reported by Goerdeler. The acyl isothiocyanates are of lower energy than the thioacyl isocyanates, but in many cases an equilibrium between the two is achievable.

Introduction

In recent work we have investigated a series of thermal 1,3-shifts interconverting α-oxoketenes[1] (**1a**≡**2a**; a degenerate rearrangement in this case), imidoylketenes and oxoketenimines[2] (**1b** and **2b**), and vinylketenes and acylallenes[3] (**1c** and **2c**),[4] eqn. (1).



(1)

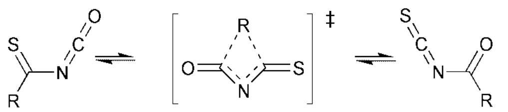
1 **2**

a X = O
b X = NH
c X = CH_2
d X = S

Moreover, we have recently reported the analogous acylthioketene–thioacylketene rearrangement (**1d** and **2d**).[5] Our calculations using *ab initio* and density functional theory (DFT) methods have revealed that these migrations are highly facilitated by electron-donating migrating groups, especially when a lone pair on the migrating group or atom is able to interact with the low-lying in-plane LUMO of the ketene moiety.[1b,6] Thus, the order of migration aptitudes in α-oxoketenes (**1**) at the G2(MP2,SVP) level of theory is: NMe_2 (34) > Br (39) > SCH_3 (47) > SH (52) > Cl (53) > PH_2 (59) > NH_2 (70) > F (89) > OCH_3 (98) > OH (115) > SiH_3 (120) > H (143) ⩾ CH_3 (206) (calculated activation energy barriers in kJ mol^{-1}).[1b] It is seen that groups such as NMe_2, MeS, Cl, and MeO will undergo this 1,3-shift in acylketenes below or near room temperature. This was recently demonstrated experimentally for the 1,3-Cl shift in chlorocarbonyl(phenyl)ketene, which takes place at −30 °C with an activation barrier of 41.8 kJ mol^{-1} (10 kcal mol^{-1}).[1b]

These reactions can also be looked upon as pseudopericyclic[7,8] reactions. Lemal[7] defined pseudopericyclic reactions as those where there is a disconnection in the loop of interacting orbitals. This is typically the case when bonding and nonbonding (lone pair) orbitals change roles. Pseudopericyclic reactions are not bound by the Woodward–Hoffmann rules of orbital symmetry, and all reactions become allowed, regardless of the number of electrons. Whereas suprafacial 1,3-shifts are thermally forbidden by the Woodward–Hoffmann rules, as substantiated by a very high calculated barrier for the 1,3-H shift in propene,[9] such shifts become allowed in ketenes because of the presence of orthogonal orbitals.[1a] In other words, the reactions become pseudopericyclic. As mentioned above, a favourable lone pair–LUMO interaction makes these pseudopericyclic reactions extremely facile.

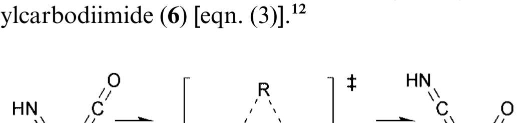
Starting in the 1960s, Goerdeler and his students reported the isomerisation of thioacyl isocyanates (**3**) to acyl isothiocyanates (**4**) [eqn. (2)], which takes place in solution at temperatures around 100 °C.



(2)

3 **4**

The acyl isothiocyanates (**4**) are the more stable, but in favourable cases an equilibrium between the two may be approached from either side.[10] The qualitative migratory aptitudes of the group R were: $(Alk)_2N$, Alk(Ar)N > ArS > AlkS ⩾ ArO > AlkO, whereby the fast rates of the arylated functions was considered abnormal and unexplained. No rearrangement took place when R = aryl, *tert*-butyl, or CCl_3.[11] From the available kinetic data,[10e,11] one can estimate an activation barrier for the dimethylamino group migration (**3**, R = NMe_2) of $\Delta G^‡ \sim 107$ kJ mol^{-1} and a free energy difference $\Delta G^\circ \sim 7$ kJ mol^{-1} favouring the isothiocyanate (**4**, R = NMe_2). It is emphasised that the authors described the kinetics as "complicated" and therefore the above-derived energy values should be taken as a guide only. Goerdeler and Raddatz also described an isomerisation of an imidoyl isocyanate (**5**) to an acylcarbodiimide (**6**) [eqn. (3)].[12]



(3)

5 **6**

All these Goerdeler rearrangements are similar to the ketene-type rearrangements described above [eqn. (1)]. In order to better understand the migratory aptitudes, activation barriers, and orbital interactions governing rearrangements of these types, we have carried out *ab initio* calculations on the isocyanate–isothiocyanate rearrangement [eqn. (2)] and report

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† Supplementary data containing all calculated energies and geometries of all structures are available. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b003534n

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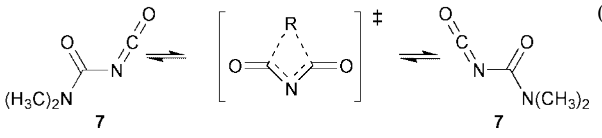
the results herein. Additional calculations on dimethylamido isocyanate (**7**) are included for the purpose of comparison with the degenerate isocyanate–isocyanate interconversion[1b] [eqn. (4)].



(4)

Computational methods

Standard *ab initio* molecular orbital calculations[13] were carried out using the GAUSSIAN 94 system of programs.[14] Geometry optimisations of all structures were performed with the standard polarised split-valence 6-31G* basis set at the Hartree–Fock (HF), second-order Møller–Plesset pertubation (MP2) and the density functional theory B3LYP[15] levels. Harmonic vibrational frequencies were calculated at the HF/6-31G* level in order to characterise the stationary points as minima and transition state structures and to evaluate zero-point vibrational energies (ZPVEs). The directly calculated ZVPEs were scaled by 0.9135 to account for their overestimation at this level of theory.[16] Improved energies were obtained at the G2(MP2,SVP) level of theory.[17] This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* energies together with zero-point vibrational and isogyric corrections. In the G2(MP2,SVP) theory, the basis-set extension energy contribution is calculated at the MP2 level and the QCISD(T) energy is evaluated using the 6-31G* basis set. It has been shown that the accuracy of the G2(MP2, SVP) method is comparable to that of the G2(MP2)[18] theory but computationally more efficient. The frozen-core approximation was employed for all correlated calculations. For the evaluation of thermochemical data, additional frequency calculations were performed at the MP2/6-31G* level of theory.

Results and discussion

Relative stabilities of isomers

In general, both the thioacyl isocyanates (**3**) and the acyl isothiocyanates (**4**) can exist as a mixture of two conformers: s-*trans* and s-*cis*.[19] The calculations usually reveal a preference for the s-*cis* isomer in both cases, being more dominant for the thioacyl isocyanates (by 0.9–10.0 kJ mol^{-1}) than for the acyl isothiocyanates (by −4.6–3.2 kJ mol^{-1}). Only in two instances, the chloro- and bromo-substituted acyl isothiocyanates, are the s-*trans* structures energetically favoured. In previous computational work we found that different substituents may stabilise either the s-*cis* or the s-*trans* form of acylketenes, acylketenimines, imidoylketenes, and vinylketenes within a ~10 kJ mol^{-1} range.[4,6] We should mention that for some of the s-*trans* conformers no minima could be located. Starting from a planar s-*trans* geometry, they rotate during the optimisation around the central single bond to yield the more stable s-*cis* isomers. This occurs for both the thioacyl isocyanates and acyl isothiocyanates with R = NH_2 and $N(CH_3)_2$. The thiocarbamoyl isocyanate can be located at HF/6-31G* but disappears at the correlated level, indicating a very shallow minimum at the former level. The two conformers of the thioacyl isocyanates are always less stable than the corresponding acyl isothiocyanates, the difference usually 10–20 kJ mol^{-1}. This is in agreement with the above-mentioned observations made by Goerdeler. In the following discussion of activation energies we will focus on the s-*cis* forms of thioacyl isocyanates and acyl isothiocyanates, although they have to rotate around the C–N single bond in order allow migration of the substituent R. They are clearly the more stable isomers and can be optimised for all the investigated substituents.

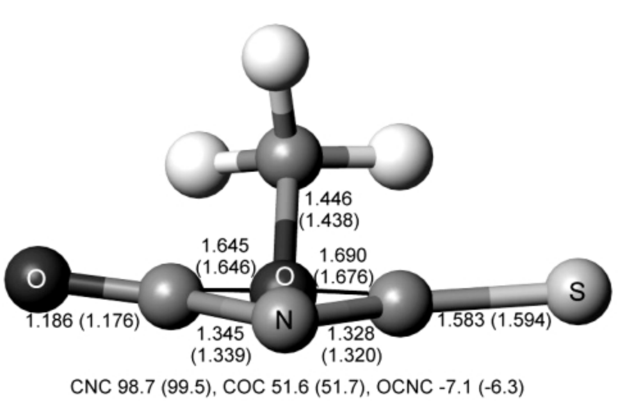


Fig. 1 MP2/6-31G*-optimised transition state structure of methoxycarbonyl isothiocyanate–methoxy(thioacyl) isocyanate rearrangement (B3LYP/6-31G* values in brackets, bond lengths in Å, angles in °).

Activation barriers and free energy calculations

The activation barriers calculated for the exothermic isomerisation of the eleven substituted thioacyl isocyanates to yield the corresponding acyl isothiocyanates lie in the range 75–285 kJ mol^{-1}, the relative ordering being $Br < Cl < N(CH_3)_2 < F$, SCH_3, $SH < OCH_3$, $NH_2 < OH \ll H \ll CH_3$. Obviously, the energies required for the reverse step are higher (100–300 kJ mol^{-1}), but the relative ordering is qualitatively the same. The migratory aptitudes of these substituents are consistent with experimental and theoretical results for related systems.[6]

Density functional theory calculations were included in order to assess the performance of the computationally much less demanding B3LYP approach (compared to the G2 theories). In general, the energy ordering and activation barriers are nearly identical for the two methods. Differences between G2(MP2,SVP) and B3LYP/6-31G* energies are very small, with the exception of the chlorine and bromine migrations. Here, the DFT-determined barriers are about 15 kJ mol^{-1} lower, thus indicating a need for care when studying halogenated systems with these methods. Structural data of a MP2- and B3LYP-optimised transition state are given in Fig. 1. It can be clearly seen that both geometries are comparable and that the central “core” formed by C–N–C and the migrating oxygen atom is indeed planar.

Another substituent of interest is the S–Ph group. Although the resulting system is too large to be evaluated at the G2(MP2,SVP) level, reliable information is obtained at the MP2/6-31G* and B3LYP/6-31G* levels. The predicted activation barrier of 115 (108) kJ mol^{-1} is slightly lower than those for the other sulfur-containing substituents (SH, SMe), and of the same order as the barrier for the dimethylamino group.

The calculation of the degenerate rearrangement of **7** yields an activation energy of 100 kJ mol^{-1}, *i.e.* 12 kJ mol^{-1} less than the barrier in the corresponding thioacyl isocyanate. This is in accordance with other theoretical work, where the activation barriers for several acyl isocyanates (H: 207, F: 116, Cl: 84.5, Br: 72 kJ mol^{-1}) are given.[1b] All computed migration energies are slightly lower in the acyl isocyanates than in the thioacyl isocyanates. This can be attributed to the C=S group being less electron withdrawing than C=O; accordingly the LUMO of **3** is higher in energy (3.02 eV, R = H, HF/6-31G*) than that of **7** (2.77 eV, R = H), and the interaction with an electron donating migrating group is correspondingly weaker.

Furthermore, we have extended our investigation to the calculation of entropies and Gibbs free energies for the dimethylamino system in order to compare these data with the energies given by Goerdeler. The calculated (MP2/6-31G*) preference of the acyl isothiocyanate over the thioacyl isocyanate of 5.9 kJ mol^{-1} is close to the experimental value of 7 kJ mol^{-1} (the computational data is given in Table S2 in the electronic supplementary data). The estimated barriers for the migration

Table 1 Relative energies (in kJ mol^{-1}) of calculated thioacyl isocyanates **3**, acyl isothiocyanates **4** and (dimethylamido)isocyanate **7**

	HF/6-31G*	MP2/6-31G*	MP2/ 6-311 +G(3df,2p)	QCISD(T)/ 6-31G*	**G2 (MP2,SVP)**[b]	B3LYP/ 6-31G*
R = H						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	13.0	8.8	7.4	9.6	**8.2**	8.0
s-*cis*-SCN–C(O)R	3.2	−6.9	−7.4	−4.8	**−5.4**	−6.5
s-*trans*-SCN–C(O)R	5.6	−3.9	−7.1	−0.6	**−3.8**	−4.3
TS	322.2	252.5	232.1	255.9	**235.5**	241.6
R = CH_3						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	17.4	9.7	8.2	11.1	**9.0**	9.6
s-*cis*-SCN–C(O)R	−8.0	−13.8	−12.5	−13.3	**−13.2**	−17.6
s-*trans*-SCN–C(O)R	−5.1	−9.8	−12.2	−7.7	**−11.7**	−12.7
TS	388.1	306.8	287.7	311.5	**284.4**	293.7
R = OH						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	10.1	4.9	6.6	4.9	**5.8**	4.9
s-*cis*-SCN–C(O)R	−17.0	−26.4	−23.5	−25.9	**−23.6**	−23.9
s-*trans*-SCN–C(O)R	−12.8	−22.2	−20.1	−21.4	**−20.4**	−19.0
TS	223.8	163.2	164.4	166.6	**161.1**	164.4
R = NH_2						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	31.6	[a]				[a]
s-*cis*-SCN–C(O)R	1.8	−12.8	−13.0	−11.9	**−14.4**	−12.6
s-*trans*-SCN–C(O)R	[a]	[a]				2.2
TS	200.8	153.1	153.0	150.4	**147.8**	151.6
R = SH						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	18.1	10.7	9.8	12.0	**10.0**	10.6
s-*cis*-SCN–C(O)R	−3.6	−15.2	−10.0	−16.0	**−11.9**	−16.5
s-*trans*-SCN–C(O)R	1.7	−10.9	−8.9	−10.0	**−9.7**	−11.0
TS	207.3	134.5	125.1	136.8	**121.8**	119.6
R = SCH_3						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	16.1	9.9	8.6	10.9	**9.7**	9.4
s-*cis*-SCN–C(O)R	−4.3	−11.0	−4.2	−13.1	**−7.2**	−14.3
s-*trans*-SCN–C(O)R	−0.8	−7.8	−4.0	−8.3	**−5.7**	−9.5
TS	197.4	136.0	125.6	136.7	**121.7**	124.3
R = F						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	9.4	3.2	6.4	3.0	**5.7**	3.4
s-*cis*-SCN–C(O)R	−31.2	−37.1	−33.5	−36.5	**−32.8**	−35.1
s-*trans*-SCN–C(O)R	−26.4	−34.6	−30.3	−33.5	**−29.5**	−32.0
TS	184.6	117.9	122.7	121.8	**121.4**	119.6
R = Cl						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	8.6	3.9	2.7	4.2	**2.7**	2.0
s-*cis*-SCN–C(O)R	−14.7	−23.1	−19.5	−23.7	**−20.6**	−26.2
s-*trans*-SCN–C(O)R	−13.2	−23.1	−22.5	−22.4	**−22.3**	−26.7
TS	137.2	96.5	91.3	99.9	**90.2**	77.0
R = Br						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	3.0	−2.3	0.7	−2.0	**0.9**	−2.6
s-*cis*-SCN–C(O)R	−12.5	−18.9	−17.3	−20.3	**−19.2**	−24.4
s-*trans*-SCN–C(O)R	−16.1	−25.6	−23.6	−25.3	**−23.8**	−29.6
TS	115.2	66.2	73.7	70.8	**74.5**	57.2
R = OCH_3						
OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	9.5	5.1	6.6	4.9	**5.8**	4.9
s-*cis*-SCN–C(O)R	−21.7	−24.8	−20.7	−25.8	**−22.3**	−26.1
s-*trans*-SCN–C(O)R	−18.4	−21.1	−17.8	−21.9	**−19.4**	−21.5
TS	196.5	143.5	145.3	146.8	**143.1**	147.9

Table 1 (*Contd*)

	HF/6-31G*	MP2/6-31G*	MP2/ 6-311 +G(3df,2p)	QCISD(T)/ 6-31G*	**G2 (MP2,SVP)**[b]	B3LYP/ 6-31G*
R = $N(CH_3)_2$						
s-*cis*-OCN–C(S)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(S)R	[a]	[a]				[a]
s-*cis*-SCN–C(O)R	−1.8	−9.6	−6.1	−10.8	**−9.1**	−15.5
s-*trans*-SCN–C(O)R	[a]	[a]				[a]
TS	164.8	119.5	117.5	117.0	**111.8**	125.2
R = $N(CH_3)_2$						
s-*cis*-OCN–C(O)R	0.0	0.0	0.0	0.0	**0.0**	0.0
s-*trans*-OCN–C(O)R	[a]	[a]				[a]
TS	145.0	106.1	101.1	106.0	**99.8**	116.8
R = SPh						
s-*cis*-OCN–C(S)R	0.0	0.0				0.0
s-*trans*-OCN–C(S)R	13.9	−0.4				5.8
s-*cis*-SCN–C(O)R	−3.3	−12.0				−13.8
s-*trans*-SCN–C(O)R	−1.5	−13.7				−8.6
TS	185.5	118.4				108.4
R = NMePh						
s-*cis*-OCN–C(S)R						0.0
s-*trans*-OCN–C(S)R						[a]
s-*cis*-SCN–C(O)R						−20.0
s-*trans*-SCN–C(O)R						[a]
TS						115.2
R = OPh						
s-*cis*-OCN–C(S)R						0.0
s-*trans*-OCN–C(S)R						11.9
s-*cis*-SCN–C(O)R						−28.2
s-*trans*-SCN–C(O)R						−15.9
TS						125.1

[a] Structure could not be located. [b] Zero-point vibrational energies included.

of the $N(CH_3)_2$ group are also in good agreement (118 *vs.* 107 kJ mol^{-1}), taking into account the "complicated" nature[10e,11] of the experimental data.

MO description of the rearrangement

In order to gain a qualitative understanding of the above finding, we have examined the orbital interactions which control the rearrangement. It is seen that substituents with unshared pairs of electrons are good migrators, which is understood in terms of the favourable interaction between the lone pair of the migrating group and the vacant central carbon p orbital of the iso(thio)cyanate LUMO. Thus, the above ordering predicts bromine and chlorine to be the best migrators. This computed trend should be identifiable when one examines the sets of interacting orbitals. The iso(thio)cyanate LUMO energies for different substituents however show no regularity with respect to the ease of migration. One can expect that the energy of the vacant carbon p orbital varies only little when changing the migration group. A more promising approach is the study of the appropriate migrating group lone pair. Ideally, this orbital lies in the molecular plane. In the cases of the amino substituents however, these orbitals are highly conjugated with the C=S (C=O) moieties and are therefore perpendicular to the molecular plane. The energetic ordering (in a.u.) of the lone pair orbitals in thioacyl isocyanates is computed as follows: Br $(-0.447) <$ Cl $(-0.495) <$ SCH_3 $(-0.502) <$ F $(-0.523) <$ $N(CH_3)_2$ $(-0.530) <$ OCH_3 $(-0.543) <$ SH $(-0.544) <$ NH_2 $(-0.578) <$ OH (-0.583). The conjugation of the amino groups leads to a stabilisation of the p orbital. We calculated the amount of energy required to rotate and decouple this p orbital to be 73 kJ mol^{-1} or 0.028 hartrees. Taking this energy into account increases the p orbital energies for $N(CH_3)_2$ to -0.502 and for NH_2 to -0.550 hartrees. With the exception of the SH substituent, the series of p orbital energies now follows the calculated ordering of migration aptitudes (Fig. 2). Neither the methyl group nor the hydrogen atom possess the necessary p orbitals and therefore cannot form the favourable interactions, resulting in much higher migration barriers.

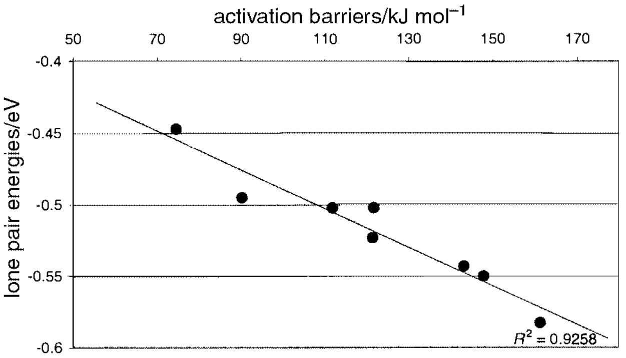


Fig. 2 Correlation of rearrangement activation barriers with energies of lone pair orbitals, corrected values for amino substituents (see text for details).

The DFT study was extended to aryl-substituted compounds (R = SPh, OPh and NPhMe) as G2 or other correlated methods are not feasible. The Becke3LYP approach was shown above to give reliable results for iso(thio)cyanates and is therefore employed as the method of choice. From the results in Table 1, it can be seen that the introduction of an aryl group lowers the activation barrier for the migration by 10–22 kJ mol^{-1}; Goerderler's observed acceleration of the rearrangement[10] is confirmed. One reason for the improved migration ability of aryl-substituted iso(thio)cyanates can be seen in the different lone pair energies of alkyl and aryl systems. They differ at the applied Becke3LYP/6-31G* level by about 0.005–0.01 au (13–26 kJ mol^{-1}), with the aryl group-bearing iso(thio)cyanates having the more reactive lone pairs.

Conclusion

In good agreement with experimental data, the order of migratory aptitudes for the pseudopericyclic title rearrangement is computed at the G2(MP2,SVP) level of theory as $\mathrm{Br} > \mathrm{Cl} > \mathrm{NMe_2} > \mathrm{F}$, $\mathrm{SCH_3}$, $\mathrm{SH} > \mathrm{OMe}$, $\mathrm{NH_2} > \mathrm{OH} \gg \mathrm{H} \gg \mathrm{Me}$, with energy barriers between 75 and 285 kJ mol^{-1}. Acyl isothiocyanates are found to be more stable than the corresponding thioacyl isocyanates. These findings are confirmed at the computationally much less demanding Becke3LYP/6-31G* level, which is also successfully applied to several larger aryl-substituted iso(thio)cyanates. The lone pair energies of the iso(thio)cyanates serve as a satisfactory explanation of the calculated and observed reactivity sequence. They correlate well with the activation barriers.

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