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Studies of Polarized Ethylenes. Part X.* Activation Enthalpies and Entropies to Rotation Around the Carbon-Carbon Double Bond in Two Ketene Mercaptals

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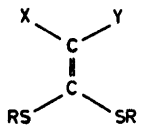
The thermodynamic parameters for the rotation around the carbon-carbon double bond in 3,3-bismethylthio- and 3,3-bisbenzylthio-2-nitroacrylonitrile have been measured by the complete bandshape method over temperature intervals of 86 and 48 °C, respectively. The barriers are quite low with $\Delta H^{\ddagger} = 54.9$ and 59.3 kJ mol^{-1} respectively, and the activation entropies are negative, −63 and −60 J mol^{-1} K^{-1}, as expected for a process with a polar transition state. The higher barrier in the benzyl compound is in agreement with the known inductive effects of the methyl and benzyl groups, but it is in opposition to ionization energies from photoelectron spectra and also to the order between the barriers in a similar pair of ketene mercaptals.



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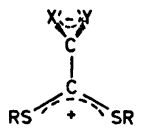

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	X	Y	R
1a	O_2N,	CN	CH_3
1b	O_2N	CN	CH_2Ph
1c	PhCO	$COCH_3$	CH_3
1d	PhCO	CN	CH_3
1e	CH_3OCO	CN	CH_3
1f	CH_3OCO	CN	CH_2Ph
1g	H_2NCO	CN	CH_3
1h	C_2H_5OCO	COPh	CH_3

The free energy barrier to rotation around the carbon-carbon double bond in ketene mercaptals substituted with acceptor groups (*1*) decreases with increasing capacity of the acceptor groups to stabilize a negative charge.[1] The activation entropy for the rotation was found to be strongly negative, values between −50 and −100 J mol^{-1} K^{-1} being observed.[1-4] These observations have been interpreted in terms of a rotational process with a dipolar transition state (*2*). In *1* as well as in *2* the stabilization will depend on the acceptor capacity of X and Y, but the interaction with the negative charge in *2* is expected to be more strengthened by increasing acceptor capacity than the interaction with the neutral donor groups (RS) in *1*. Therefore the transition state will be lowered more than the ground state by increased acceptor capacity. The conjugation in the ground state leads to a moderate charge transport, whereas the transition state will be considerably more polarized, even if the complete charge separation depicted by *2* may not take place.[5] In the ground state the solvent molecules will already be somewhat oriented with respect to the molecular dipoles of the solute molecules, and in the transition state this orientation will be reinforced by the increased dipole moment, which has the same direction as the ground state moment. This will lead to a higher degree of order in the transition state and thus to a negative entropy of activation. In general, polarized ethylenes with high barriers have less polar ground states than such with low barriers,

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and therefore an increasingly negative activation entropy should accompany an increase in rotational barrier.

Negative activation entropies are as a rule observed in reactions where neutral molecules react to give transition states with charge separation, and the creation of a pair of unit charges is known to give contributions to $\Delta S^{\ddagger}$ in the range -40 to -120 J mol^{-1} K^{-1}, depending on solvent polarity and charge distribution,[6] the effect being larger with more concentrated charges.[7]

The present study was undertaken with three purposes:

1. To measure the barrier in ketene mercaptals with a new and powerful combination of acceptor groups, and to correlate the effect of the substituents with those observed in analogous compounds.

2. To make a careful determination of the activation entropy.

3. To compare the effect on the rotational barrier of methylthio and benzylthio groups as donors.

The compounds chosen for this study are *1a* and *1b*, which are available through the well-known condensation between carbon disulfide and anions of CH-acidic compounds. However, contrary to previous results with cyano stabilized carbanions,[8] but in analogy with nitroethane [9] the condensation of carbon disulfide with the anion of nitroacetonitrile gave only a very low yield of product.

EXPERIMENTAL

Preparative part

3,3-Bismethylthio-2-nitroacrylonitrile (1a). Carbon disulfide (0.05 mol) and triethylamine (0.05 mol) were added to a solution of the ammonium salt of nitroacetonitrile [10] (0.05 mol) in hexamethylphosphoric triamide (100 ml). The mixture was stirred for 30 min at room temperature, whereupon methyl iodide (0.10 mol) was added and the stirring continued for 2 h. Water (50 ml) was added and the mixture was extracted with toluene. The washed and dried toluene phase was filtered through a short column containing alumina (Woelm W 200 neutral, 10 g). The eluate was concentrated *in vacuo* and the residue was recrystallized from toluene–hexane to give *1a* as light yellow crystals in 7 % yield, m.p. 102–103 °C, M.W. (mass spectroscopy) 190. Anal. $C_5H_6N_2O_2S_2$: C, H, N.

3,3-Bisbenzylthio-2-nitroacrylonitrile (1b) was prepared in the same way, substituting benzyl bromide for methyl iodide. Yield 15 %, m.p. 92–93 °C, M.W. 342. Anal. $C_{17}H_{14}N_2O_2S_2$: C, H, N.

Spectroscopic part

The ^1H NMR spectra were recorded on a JEOL MH-100 spectrometer equipped with standard variable temperature probe and temperature controller. The spectra were recorded on 0.5 M solutions of *1a* and *1b* in *o*-dichlorobenzene (ODC), containing *ca* 5 % of hexamethyldisiloxane (δ 0.100) to give the signal for the internal lock. The temperatures were determined as described in Ref. 11, and the transverse relaxation times by the method laid out in Ref. 12, using the linewidths of the methyl resonances of dimethyl phthalate (for *1a*) and acetophenone (for *1b*), respectively, as resolution probes. The benzylic methylene proton resonances were broadened by unresolved long-range couplings to the aromatic protons, but they were still reasonable Lorentzian in shape, and it was regarded as permissible to include this broadening in the effective T_2 value. The non-exchanging chemical shifts, $\Delta\nu_0$, obtained below the slow exchange limit and by band-fitting up to a temperature about 5 K below coalescence showed a fairly strong but linear variation with the temperature.

The rate constants were obtained by fitting calculated bandshapes to the experimental ones, varying the rate constant, k, and $\Delta\nu_0$ below the coalescence temperature and k alone above the coalescence temperature. In this temperature region the $\Delta\nu_0$ values were obtained by extrapolation of a least squares plot of the low-temperature values *versus* temperature. The theoretical bandshapes were calculated on a Hewlett Packard Model 9820 A desk calculator equipped with a Model 9862 A plotter, using the simple McConnell equation for an uncoupled two-site exchange.[13] The activation enthalpies and entropies were obtained from a linear least squares plot of log k/T *versus* $1/T$ using the Eyring equation [14] in the form (1).

$$\log (k/T) = -\Delta H^{\ddagger} \log e/RT + \Delta S^{\ddagger} \log e/R + \log (k_B/h) \quad (1)$$

The photoelectron spectra were recorded on a Perkin-Elmer Model PS 18 photoelectron spectrometer, and they were calibrated using the Ar and Xe lines. Reproducibility was ± 0.03 eV.

RESULTS AND DISCUSSION

The rate constants and barriers are found in Tables 1 and 2, and the corresponding Eyring plots are shown in Fig. 1.

Table 1. Rate constants and free energy barriers for *1a*.

T/K	$T_{\frac{1}{2}}$/s	k/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
310.0	0.397	1.54	74.87
314.7	0.412	2.35	74.94
319.4	0.389	3.40	75.12
324.8	0.369	5.00	75.39
329.3	0.404	6.60	75.71
334.1	0.412	8.70	76.09
339.3	0.404	13.7	76.04
343.3	0.376	17.2	76.32
348.4	0.412	20.6	76.97
354.8	0.438	32.5	77.10
357.4	0.376	34.5	77.51
361.2	0.456	40.0	77.92
366.5	0.488	53.0	78.25
371.7	0.429	69.0	78.59
375.4	0.447	85.0	78.75
381.2	0.404	114.0	79.09
386.2	0.408	133.0	79.67
391.6	0.499	182.0	79.81
396.8	0.488	250.0	79.86

$\Delta H^{\ddagger} = 54.9 \pm 0.6$[a] kJ mol^{-1}
$\Delta S^{\ddagger} = -63 \pm 2$ J mol^{-1} K^{-1}

[a] The errors are standard deviations from the least squares plot.

Table 2. Rate constants and free energy barriers for *1b*.

T/K	$T_{\frac{1}{2}}$/s	k/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
332.7	0.251	2.11	79.68
336.7	0.270	3.20	79.50
342.6	0.260	4.65	79.88
346.2	0.277	6.70	79.70
351.4	0.260	8.40	80.28
356.1	0.277	10.5	80.73
360.9	0.254	13.3	81.15
366.1	0.274	20.1	81.11
371.0	0.267	27.0	81.33
376.0	0.235	32.5	81.88
380.9	0.245	35.5	82.69

$\Delta H^{\ddagger} = 59.3 \pm 1.8$ kJ mol^{-1}
$\Delta S^{\ddagger} = -60 \pm 5$ J mol^{-1} K^{-1}

Shvo *et al.*[4] have shown that the logarithms of the first-order constants for the rates of topomerization in three series of push-pull ethylenes with different donor groups could be correlated with the σ_R^- values for one of the

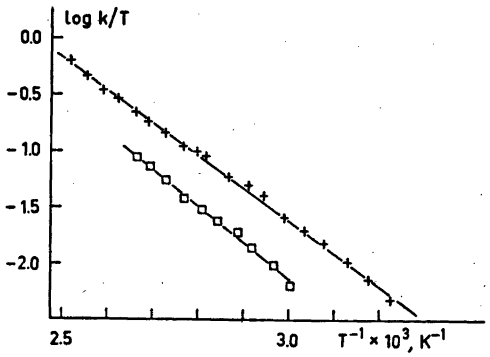

Fig. 1. Eyring plots for *1a* (+) and *1b* (□).

acceptor groups while keeping the other acceptor group constant, whereas no linear behaviour was observed when the log k values were plotted *versus* the sums of the σ_R^- values.

We have tried similar correlations with the methylthio derivatives *1a*, *1c*–*1e*, *1g* and *1h*. For three of these compounds (*1a*, *1c*,[15] and *1d*[1]), activation entropies have been evaluated, and for the others they can be estimated with reasonable accuracy. The activation entropy for the *S*-methyl-*S*-benzyl analogue of *1e* has been found to be -100 J mol^{-1} K^{-1} in deuteriochloroform solution,[1] and it is assumed to be nearly the same for *1e* and *1f* in ODC. Shvo *et al.*[4] have shown that $\Delta S^{\ddagger}$ for one push-pull ethylene becomes more negative with increasing solvent polarity, but the polarities of $CDCl_3$ and ODC are so similar that no great difference in $\Delta S^{\ddagger}$ is to be expected. No data for *1h* are available, but its $\Delta S^{\ddagger}$ value is assumed to be -74 J mol^{-1} K^{-1}, intermediate between the values for *1c* and *1d*. The log k values used for the correlations (Table 3) have been calculated at 398 K, a temperature close to or in the regions where the $\Delta S^{\ddagger}$ values have been found.

The σ_R^- values are obtained from the relation $\sigma_R^- = \sigma^- - \sigma_I$,[16] and the σ_I and σ_R^- values are taken from the recent critical collection by Exner.[17] Since no parameters for the benzoyl group are available, those for the acetyl group have been used instead.

No reasonable linear behaviour is shown when log k_{378} for *1a*, *1d*, *1e* and *1g*, which all have one CN group as a common acceptor, is plotted *versus* the σ_R^- values for the other acceptor group. When log k_{398} for all six com-

Table 3. Thermodynamic and rate data for correlation with $\Sigma\sigma_R^-$ values.

Compound	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	log k_{308}	$\Sigma\sigma_R^-$	Ref.
1a	54.9	−63	2.44	0.63	This work
1c	49.6	−76	2.44	0.90	15
1d	57.7	−72	1.58	0.64	1
1e	57.6[a]	−100[b]	0.13	0.43	1
1g	57.8[a]	−100[b]	0.11	0.45	—
1h	53.4[a]	−74[b]	2.05	0.69	—

[a] Estimated from $\Delta G^{\ddagger}$ at the coalescence and the assumed $\Delta S^{\ddagger}$ value. [b] See text.

pounds is plotted *versus* $\Sigma\sigma_R^-$, it is found that all except *1a* fall reasonably close to a straight line (correlation coefficient 0.96), whereas the log k value for *1a* is far too high for its $\Sigma\sigma_R^-$ value. Taft [18] has shown that log k for the rate of carbanion formation in a series of substituted methanes, a reaction which has a more than superficial resemblance to the one studied here, can be satisfactorily correlated with the quantity $26.0\,\sigma_R^- + 4.0\,\Sigma\sigma_I$. Since this relation cannot correlate data from compounds with two strong acceptor groups, and since two-parameter linear free energy relations in general are of questionable value,[19] no quantitative treatment of our data along these lines has been attempted. It is obvious, however, that the barrier-lowering effect of the nitro group in ketene mercaptals is underestimated by the current σ_R^- values.

The activation entropies for *1a* and *1b* are the same within the limits of error. They do not differ significantly from that of *1d* ($\Delta S^{\ddagger} = -72 \pm 6$ J mol^{-1} K^{-1}),[1] and they fit well into the general picture given in the introduction.

An unexpected result is the difference of *ca* 4 kJ mol^{-1} between the barriers of *1a* and *1b*, the comparison between *1e* and *1f* having earlier given a difference of *ca.* 3 kJ mol^{-1} in the opposite direction.[1]

The higher barrier in *1b* could indicate a lower donor capacity of the benzylthio than of the methylthio groups, in agreement with the Hammett σ_m and σ_p values for the methyl and benzyl groups ($\sigma_m = -0.062$ and -0.047, $\sigma_p = -0.135$ and -0.058, respectively).[20] This, however, does not apply to the ground state, since the photoelectron spectra of *1a* and *1b* show the benzylthio groups to be the *better* donors (Table 4). The pholoelectron spectra of 1,1-dicyanoethylenes with two sulfur-containing donor groups in position 2 have recently been analyzed.[21] The first band (*ca.* 9 eV) was ascribed to the highest bonding π-orbital (π_1) and the second band (*ca.* 10 eV) to the antisymmetric combination of the donor atom p_z orbitals (n_-). The spectrum of *1a* can be assigned similarly, since the two first IPs of simple nitro compounds fall in the range 11 – 12 eV [22] and are assigned to orbitals which for symmetry reasons cannot interact strongly with the π_1 and n_- orbitals of the NC–C=C(SR)$_2$ moiety. The spectrum of *1b* shows an intense band at 9.2 eV due to the four approximately degenerate benzene π orbitals. However, shoulders on the lower and upper sides of this band are assigned to the π_1 and n_- orbitals of the NC–C=C(S–)$_2$ system, respectively. As seen in Table 4, these IE's are lower for *1b* than for *1a*.

Summing up, the order of the barriers of *1a* and *1b* is as expected from the inductive effects of the methyl and benzyl groups, whereas the barriers of *1e* and *1f* and the photoelectron spectra of *1a* and *1b* point at a reversed order of donor effect. We have at present no explanation to offer for this apparent anomaly.

Table 4. Photoelectron spectra of *1a* and *1b*.

Compound	IE eV	Assignment
1a	9.18	π_1
	9.73	n_-
1b	8.7 (shoulder)	π_1
	9.55	n_-

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REFERENCES

1. Sandström, J. and Wennerbeck, I. *Acta Chem. Scand. 24* (1970) 1191.
2. Isaksson, G. and Sandström, J. *Acta Chem. Scand. 27* (1973) 1183.
3. Kalinowski, H.-O., Kessler, H. and Walter, A. *Tetrahedron 30* (1974) 1137.
4. Belsky, I., Dodiuk, H. and Shvo, Y. *J. Org. Chem. 42* (1977) 2734.

5. Ericsson, E., Marnung, T., Sandström, J. and Wennerbeck, I. *J. Mol. Struct. 24* (1975) 373.
6. Hoffmann, R. W. *Aufklärung von Reaktionsmechanismen*, Thieme, Stuttgart 1976, p. 40.
7. Frost, A. A. and Pearson, R. G. *Kinetics and Mechanism*, Wiley, New York 1960, p. 129.
8. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand. 22* (1968) 1107.
9. Gompper, R. and Schaefer, H. *Chem. Ber. 100* (1967) 591.
10. Steinkopf, W. and Bohrmann, L. *Ber. Dtsch. Chem. Ges. 41* (1908) 1044.
11. Lidén, A., Roussel, C., Liljefors, T., Chanon, M., Carter, R. E., Metzger, J. and Sandström, J. *J. Am. Chem. Soc. 98* (1976) 2853.
12. Lidén, A. and Sandström, J. *Tetrahedron 27* (1971) 2893.
13. McConnell, H. M. *J. Chem. Phys. 28* (1958) 430.
14. Glasstone, S., Laidler, K. J. and Eyring, H. *Theory of Rate Processes*, McGraw-Hill, New York 1941, p. 195.
15. Berg, U. and Sjöstrand, U. *Org. Magn. Reson. In press.*
16. Taft, R. W., Jr. In Newman, M. S., Ed., *Steric Effects in Organic Chemistry*, Wiley, New York 1956, Chapter 13, pp. 578, 599.
17. Exner, O. In Chapman, N. B. and Shorter, J., Eds., *Advances in Linear Free Energy Relationships*, Plenum, London 1972, Chapter 1, p. 21.
18. Taft, R. W., Jr. *J. Am. Chem. Soc. 79* (1957) 5075.
19. Ref. 17, p. 39.
20. Sjöström, M. and Wold, S. *Chem. Scr. 9* (1976) 200.
21. Betteridge, D., Henriksen, L., Sandström, J., Wennerbeck, I. and Williams, M. *Acta Chem. Scand. A 31* (1977) 14.
22. Rao, C. N. R. *Indian J. Chem. A 14* (1976) 147.

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