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Barriers to Ring Reversal of 5- and 6-Membered Cyclic Ketyl and Thioketyl Radical Anions

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The barriers to the ring reversal process of cyclopentanone, cyclopentanethione, cyclohexanone and cyclohexanethione, radical anions were determined by line-shape analysis of their low-temperature ESR spectra in solution. The free energies of activation for the 5- and 6-membered ketyl (2.7 and 6.3 and kcal mol^{-1}, respectively) were found similar to those of the corresponding thioketyl radical anions (2.9 and 5.7$_5$ kcal mol^{-1}, respectively) but higher than those of the related molecules cyclopentanone and cyclohexanone (2.0 and 4.0 kcal mol^{-1}, respectively).

Hydrogen abstraction from the α-carbon of primary alcoholates and thiolates carried out by means of a photolitic reaction yields the corresponding aldehyde and thioaldehyde radical anions.[2−6] The same reaction applied to secondary alcoholates[5] and thiolates[6] was reported to yield the corresponding ketyl and thioketyl radical anions in conditions suited for detecting their ESR spectra. Cyclohexanone ($\mathbf{1}^{\bullet-}$) and cyclohexanethione ($\mathbf{2}^{\bullet-}$) radical anions displayed ESR spectra with alternating line width effects due to ring reversal of the 6-membered ring.[5,6] In the case of $\mathbf{1}^{\bullet-}$ the barrier for such a dynamic process could be determined[5,7] ($\Delta G^* = 6.1$ kcal mol^{-1}, with a negligible ΔS^*), whereas in the case of $\mathbf{2}^{\bullet-}$ the experimental conditions did not allow the analogous measurement to be obtained.[6]

We report here the determination of such a barrier for cyclohexanethione as well as for the analogous 5-membered derivatives cyclopentanone ($\mathbf{3}^{\bullet-}$) and cyclopentanethione ($\mathbf{4}^{\bullet-}$) radical anions.

Addition to the samples of cyclopropane as solvent (see Experimental Section) allowed us to reach temperature ranges much lower than previously attained so that internal motions that had so far eluded detection, because of a too low activation energy, could be monitored. In the case of $\mathbf{1}^{\bullet-}$ these experimental conditions did not apparently modify the a_H splittings, nor the free energy of activation (see Table 1), which was found equal ($\Delta G^* = 6.3 \pm 0.15$ kcal mol^{-1}), within the experimental errors, to that recently reported.[5,7] In the case of $\mathbf{2}^{\bullet-}$ we could reach temperatures (−100 °C) low enough to detect the static spectrum displaying two different a_H splittings for the pseudo-axial and pseudo-equatorial hydrogens bonded to C-2 and C-6 (i.e. 30.7 and 5.5 Gauss). The average of these values (18.1 G) corresponds to the splitting (17.9 G) found[6] at higher temperatures for the four equivalent β-hydrogens of $\mathbf{2}^{\bullet-}$.

Table 1. ESR Parameters of Radical Anions $\mathbf{1}^{\bullet-}$−$\mathbf{5}^{\bullet-}$ and The Free Energies of Activation (ΔG^*, in kcal mol^{-1}) for Ring Reversal of $\mathbf{1}^{\bullet-}$−$\mathbf{4}^{\bullet-}$

radical	T (°C)	a_H (Gauss)	g factor	ΔG^*
$(CH_2)_5C{=}O^{\bullet-}$ ($\mathbf{1}^{\bullet-}$)[a]	−80	8.4 (2H); 32.7(2H)	2.0034	6.3
$(CH_2)_5C{=}S^{\bullet-}$ ($\mathbf{2}^{\bullet-}$)[b]	−100	5.5 (2H); 30.7$_5$ (2H)	2.0051	5.7$_5$
$(CH_2)_4C{=}O^{\bullet-}$ ($\mathbf{3}^{\bullet-}$)[a]	−100	28.4 (4H)[c]	2.0035	2.7
$(CH_2)_4C{=}S^{\bullet-}$ ($\mathbf{4}^{\bullet-}$)	−100	27.5 (4H)[c]	2.0057	2.9
$(CH_2)_3C{=}O^{\bullet-}$ ($\mathbf{5}^{\bullet-}$)	−60	25.6 (4H); 0.6 (2H)	2.0037	

[a] See also ref 5. [b] See also ref 6. [c] See the text for the choice of the Δa_H values.

Line-shape analysis (Figure 1) at various temperatures (see Experimental Section) yielded rate constants corresponding to a set of ΔG^* values essentially equal to each other within the errors (5.7$_5 \pm 0.15$ kcal mol^{-1}). As in the case of $\mathbf{1}^{\bullet-}$ the free energy of activation appears, in practice, to be independent of the temperature, indicating again a negligible value for ΔS^*. Even allowing for the experimental uncertainties, the barrier to ring reversal for $\mathbf{2}^{\bullet-}$ appears lower (albeit by only 0.5 kcal mol^{-1}) than that of $\mathbf{1}^{\bullet-}$, suggesting the possibility that the 6-membered ring of the thioketyl is more flexible than the ring of the corresponding ketyl radical anion. This might reflect a slight difference in the sp^2 character[6] of the carbon of the thioketyl with respect to the carbon of the ketyl moiety.

The cyclopentanone radical anion $\mathbf{3}^{\bullet-}$ yielded, at −100 °C, a five-line spectrum with $a_H = 28.4$ G (four hydrogens). The difference with respect to the splitting reported in ref 5 (26.3 G) is most likely due to the different conditions and temperature. The analogous ESR spectrum of cyclopentanethione radical anion $\mathbf{4}^{\bullet-}$ has (at the same temperature) a slightly lower a_H splitting (27.5 G), also due to four equivalent hydrogens (Table 1). As in the case of the 6-membered radicals $\mathbf{2}^{\bullet-}$ and $\mathbf{1}^{\bullet-}$, the average splitting of the thioketyl $\mathbf{4}^{\bullet-}$ is lower than that of the ketyl radical anion $\mathbf{3}^{\bullet-}$, albeit by a much smaller amount (0.9 vs 2.4 G). Above −60 °C the widths of the signals within the spectra of $\mathbf{3}^{\bullet-}$ and of $\mathbf{4}^{\bullet-}$ are the

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[7] The original terms E_a (6.6 kcal mol^{-1}) and log A (13.2 s^{-1}) of ref 5 were translated as $\Delta G^* = 6.1$ kcal mol^{-1} and $\Delta S^* = 0.2$ eu for comparison with the present notation.

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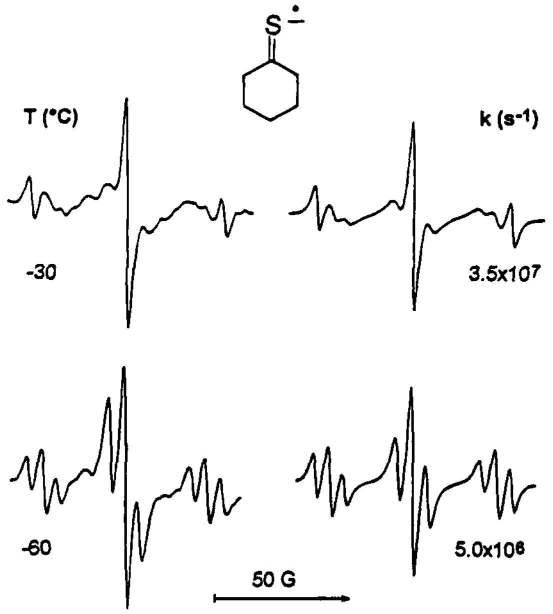

Figure 1. Experimental spectrum (left) of cyclohexanethione radical anion ($2^{\bullet-}$) at two different temperatures, showing the line broadening due to the ring reversal process. The simulations (right) were obtained with the a_H values of Table 1. The central lines of the experimental spectrum are slightly higher than expected owing to the presence of a spurious signal (see Experimental Section).

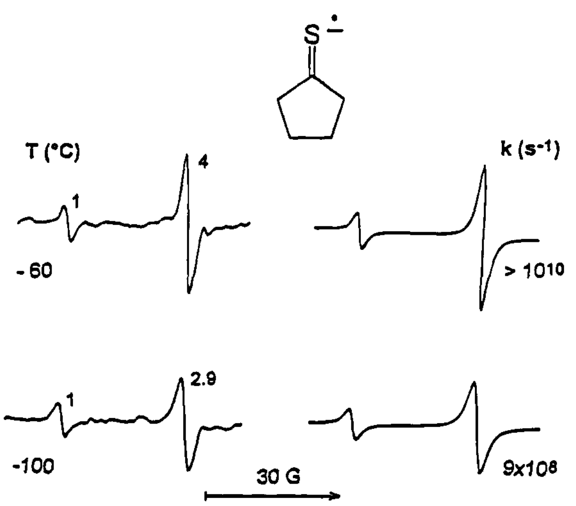

Figure 2. The first (low field) pair of lines of the experimental (left) ESR spectrum of cyclopentanethione radical anion ($4^{\bullet-}$) are displayed at two temperatures. The variation of the relative heights (1:4 at −60 °C and 1:2.9 at −100 °C), due to the ring reversal process, were simulated (right) using the a_H values (21.9 and 32.3 G) discussed in the text.

same, thus yielding lines having heights in relative ratios equal to the binomial coefficients (1:4:6:4:1). In contrast, at −100 °C and below both spectra displayed an alternating line width effect. In particular the second and fourth lines were undoubtedly broader than the first and the fifth line. As a consequence, whereas the doubly integrated intensities of the first and second line (as well as of the fourth and the fifth) still exhibit the expected 1:4 ratio, the ratio of the heights was reduced to 1:2.5 (at −120 °C in the case of $3^{\bullet-}$) and to 1:2.9 (at −100 °C in the case of $4^{\bullet-}$), as shown in Figure 2 for the first pair of low-field lines of the latter radical. Such a feature was attributed to the ring reversal process, which begins to be detectable at much lower temperatures than for the analogous 6-membered radicals. The barrier to ring reversal in 5-membered rings is known, in fact, to be much smaller than in 6-membered rings and actually a temperature where the β-hydrogens would display different splittings could not be reached. In the case of cyclopentanone radical anion $3^{\bullet-}$, however, these values are available[8] from the ESR spectrum in the solid state at −173 °C (they are 33.2 and 22.8 G). These values can be safely used, in our opinion, also for the solution spectra in that at −123 °C the solid state spectrum exhibits an average a_H value (27.8 G due to four hydrogens) nearly equal to that (28.4 G) we observed in solution at about the same temperature. Accordingly the line-shape simulation reproduced the "anomalous" 1:2.5 ratio of $3^{\bullet-}$ with a rate constant of 4×10^8 s^{-1}, corresponding to a $\Delta G^* = 2.7 \pm 0.2$ kcal mol^{-1}. The analogous pair of a_H values is not available for radical $4^{\bullet-}$, a quite reliable estimate could nonetheless be obtained. In fact the two different splittings of the 6-membered thioketyl radical anion $2^{\bullet-}$ were found smaller than those of the corresponding ketyl radical anion $1^{\bullet-}$ by amounts (2.9 and 2.0 G) almost equal to the difference between the corresponding averaged splittings (2.4 G). Since the difference between the average splittings of the 5-membered radicals $4^{\bullet-}$ and $3^{\bullet-}$ is 0.9 G, it seems conceivable to reduce by the same amount also the individual splittings[8] of $3^{\bullet-}$ and assign these values (32.3 and 21.9 G) to the β-hydrogens of $4^{\bullet-}$. The line shapes simulated with these values are shown in Figure 2: at −100 °C the rate constant[9] for ring reversal turns out to be 9×10^8 s^{-1}, corresponding to a $\Delta G^* = 2.9 \pm 0.4$ kcal mol^{-1}.

It should be outlined that the barrier measured for $3^{\bullet-}$ (2.7 kcal mol^{-1}) is larger than that of the corresponding molecule (cyclopentanone has a barrier to ring reversal[10] equal to 2.0 kcal mol^{-1}). This behavior parallels that of radical $1^{\bullet-}$ which has a barrier (6.3 kcal mol^{-1}) higher than that of cyclohexanone[11] (4.0 kcal mol^{-1}), the ratios between each pair of barriers being nearly equal (i.e. 1.4_5 ± 0.1).

A further indication that the alternating line width effect in the spectra of the 5-membered radicals ($3^{\bullet-}$ and $4^{\bullet-}$) is due indeed to a ring reversal process was derived from the observation that such an effect *does not* occur in the spectrum of cyclobutanone radical anion $5^{\bullet-}$. The latter appears as a quintet of triplets with $a_H = 25.6$ G (4 hydrogens) and $a_H = 0.6$ G (2 hydrogens). All the signals have the same line width, and accordingly, their relative heights never deviate from the expected binomial distribution, not even at −120 °C. As demonstrated by a variety of experimental determinations[12] the molecule of cyclobutanone (**5**) is planar and cannot thus undergo

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[9] We also checked that any ±1 G variation in each of the assumed a_H values which would change their difference (Δa_H) by ±2 G would affect the ΔG^* value by ±0.15 kcal mol^{-1}. Since deviations from the assumed Δa_H (i.e. 10.4 G) in excess of ±5 G seems quite unlikely, as an example, the corresponding Δa_H in $2^{\bullet-}$ (25.3 G) differs from that of $1^{\bullet-}$ (24.3 G) by as little as 1 G, the uncertainty in the ΔG^* of $4^{\bullet-}$ should not exceed ±0.4 kcal mol^{-1}.

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ring reversal processes. Recent molecular mechanics calculations[13] agree with the experiment in indicating a planar structure for **5**. Our own MM calculations[14] (carried out for *both* cyclobutanone and its radical anion) confirm that, as its parent molecule, also the cyclobutanone radical anion **5**$^{\bullet-}$ is planar, thus accounting for the absence of line width alternation in the ESR spectrum, as opposed to the case of the 5- and 6-membered analogs.

Experimental Section

The compounds used as precursors of the radical anions were all commercially available. The samples for the ESR spectra were prepared by connecting suprasil quartz tubes, containing the reactants, to a vacuum line and condensing the gaseous cyclopropane by means of liquid nitrogen; the tubes were subsequently sealed *in vacuo*. The samples were photolyzed in the cavity of the spectrometer using a 500-W high-pressure Hg lamp. The conditions yielding the ESR spectra with the more favorable signal to noise ratio are hereafter specified: **1**$^{\bullet-}$, cyclohexanol and potassium; **2**$^{\bullet-}$, cyclohexanethiol and $\mathrm{Bu^tO^-\ K^+}$; **3**$^{\bullet-}$, cyclopentanone and $\mathrm{EtO^-\ K^+}$; **4**$^{\bullet-}$, cyclopentanethiol, potassium, and $\mathrm{ButO^-\ K^+}$; **5**$^{\bullet-}$, cyclobutanol, potassium, and $\mathrm{Bu^tO{-}OBu^t}$. In the case of the thioketyl radical anions **2**$^{\bullet-}$ and **4**$^{\bullet-}$ the intensities of the central lines (see for instance Figure 1) were slightly higher than expected owing to the signal of an impurity with an almost coincident g factor. This was most evident at room temperature where the spectra of the radicals nearly disappeared, clearly revealing the line due to the spurious, unknown signal. The temperatures were measured by a thermocouple introduced in the place of the sample before and after each spectral run. This was the main source of error in the determination of the ΔG^* values, which is about ±0.15 kcal mol^{-1}, due to a ±5 °C uncertainty in the reading of the temperature. Due to the effect of the light shining on the thermocouple, this direct method is probably less accurate than the indirect one based upon the temperature dependence of the a_{H} values in a standard sample, such as that employed in ref 5. However the free energies of activation determined for the same radical (**1**$^{\bullet-}$) with both techniques yielded values (6.1 and 6.3 kcal mol^{-1}) essentially equal within the experimental errors. A minor source of error in the simulation of the spectrum of **2**$^{\bullet-}$ was a slight dependence of the line width in absence of exchange upon the quantum number.[15] Such a behavior is not uncommon in the spectra of sulfur-containing radicals taken at very low temperature,[4,16] owing to the anisotropy of their g factors. In our samples this effect began to be visible only below −90 °C, when the solution becomes quite viscous. Thus the two outer triplets (corresponding to $M = \pm 1$ for the largest splitting) display line widths slightly broader than those of the central triplet (corresponding to $M = 0$ for the largest splitting). The effect, however, decreased rapidly on raising the temperature, and could reasonably be neglected in the temperature range where the dynamic spectra of **2**$^{\bullet-}$ were simulated (six rate constants were obtained between −60 and −25 °C). Admittedly this effect might be not completely negligible in the case of **4**$^{\bullet-}$ since the simulation had to be carried out at −100 °C (Figure 2). However the larger uncertainty (±0.4 kcal mol^{-1}) in the ΔG^* value of **4**$^{\bullet-}$, due to the assumptions on the value of Δa_{H} (see ref 9), certainly encompasses the error possibly caused by this minor source of inaccuracy.

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