Mechanisms of Acid Decomposition of Dithiocarbamates. 3. **Aryldithiocarbamates and the Torsional Effect**

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Received October 11. 2001

The acid decomposition of some p-substituted aryldithiocarbamates (arylDTCs) was observed in 20% aqueous ethanol at 25 °C, $\mu = 1.0$ (KCl, for pH > 0). The pH-rate profiles showed a dumbell shape with a plateau where the observed first-order rate constant k_{obs} was equal to k_o , the rate constant of the decomposition of the dithiocarbamic acid species. The acid dissociation constants of the dithiocarbamic acids (pK_a) and their conjugate acids (pK^+) were calculated from the pH-rate profiles. Comparatively, k_0 was more than 10⁴-fold faster than alkyldithiocarbamates (alkDTCs) with similar pK_N (the acid dissociation constant of the parent amine). It was observed that the values of pK_a and pK^+ were 5 and 8 units of pK, respectively, higher than the expected values from the p K_N of alkylDTCs. The higher values were attributed to the inhibition of the delocalization of the nitrogen electron pair into the benzene ring because of the strong electron withdrawal effect of the thiocarbonyl group. Comparison of the activation parameters showed that the rate acceleration was due to a decrease in the enthalpy of activation. Proton inventory indicated the existence of a multiproton transition state, and it was consistent with an S to N proton transfer through a water molecule. There are two hydrogens contributing to a secondary SIE, and there are also two protons that are being transferred at the transition state to form a zwitterion followed by fast C-N bond cleavage. The mechanism could also be a concerted asynchronic process where the N-protonation is more advanced than the C-N bond breakdown. The kinetic barrier is similar to the torsional barrier of thioamides, suggesting that the driving force to reach the transition state is the needed torsion of the C–N bond that inhibits the resonance with the thiocarbonyl group and the aromatic moiety, increasing the basicity of the nitrogen and making the proton transfer thermodynamically favorable.

Introduction

The acid cleavages of carbamates¹⁻⁴ and monothiocarbamates¹ (eq 1) have been studied in relation to the effect of amine basicity on the reaction rate, the general acid catalysis of the expulsion of weakly basic amines, and the rate of protonation of the leaving nitrogen.



The specific acid catalysis of the decomposition of dithiocarbamates depends on the amine structure. However, dithiocarbamates derived from alkyl, aryl, and cyclic secondary amines showed different structural relationships, and consequently, it was not possible to draw conclusions about their mechanisms.¹ But recently, a detailed study of the acid cleavage of alkyldithiocarbamates⁵ concluded that the reaction occurs through two mechanisms, depending on the pK_N , the acid dissociation constant of the parent amine. At $pK_N < 10.5$, they decompose through a zwitterionic intermediate SH[±] (Scheme 1) whose N-protonation is slower than the C-N bond breakdown when $pK_N < 9.2$. At $pK_N > 9.2$, the C-N bond breakdown is the slowest step. General acid catalysis was not detected. Because of the low basicity of the nitrogen, only acids stronger than Hydron can transfer the proton in the rate-determining step.⁶ For parent amines with $pK_N > 10.5$, a new mechanism emerges that has been proposed to occur as a concerted intramolecular proton transfer and breaking of the C-N bond.⁵

The acid decomposition of aryldithiocarbamates (aryIDTCs) occurs much faster than that of alkyldithiocarbamates (alkDTCs), but no cleavage mechanism has been proposed to explain their reactivity. In this work,

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the acid decomposition of some *p*-substituted arylDTCs was studied in the acidity range from pH 4 to H_0 -5.

Experimental Section

Materials. All reagents were of analytical grade and used without further purification, except the amines that were previously distilled or crystallized in ethanol and kept at low temperature in amber bottles. Deuterium oxide (99.8% D), deuterated sodium hydroxide (40%, in D_2O), deuterated sulfuric acid (99.5% D), and EtOD (99.5% D) were purchased commercially.

p-Substituted Aryldithiocarbamates, Ammonium Salts. These were obtained by adding 110 mmol of the corresponding aniline to a solution of 25 mL of 8 M NH₄OH, 110 mmol of CS₂, and 25 mL of acetone in an Erlenmeyer flask washed with nitrogen and capped with a septum. The mixture was magnetically stirred until a maximum reading was obtained at 290 nm, and then it was allowed to crystallize. The solid was filtered, washed with cold ethanol, and dried under vacuum over phosphorus pentoxide.⁷

Phenyl: mp 97–99 °C (lit.⁷ 108–109 °C); λ_{max} 252 and 292 nm in 20% ethanol in deoxygenated water. Anal. (calcd values for C₇H₁₀N₂S₂ in parentheses): C, 45.0 (45.1); H, 5.5 (5.4); N, 15.0 (15.0); S, 34.1 (34.4). ¹³C NMR (D₂O) δ : 210.7 (CS₂), 137.5 (C-1), 125.8 (C-3,5), 123.7 (C-4), 123.0 (C-2,6).

p-Chlorophenyl: mp 93–95 °C; λ_{max} 305 and 294 nm in ethanol. Anal. (calcd values for C₇H₉N₂S₂Cl in parentheses): C, 38.4 (38.4); H, 3.9 (4.1); N, 12.3 (12.7); S, 29.3 (29.1).

p-Methoxyphenyl: mp 62–64 °C; λ_{max} 291 nm in deoxygenated water. Anal. (calcd values for C₈H₁₂N₂S₂O in parentheses): C, 44.9 (44.4); H, 5.4 (5.6); N, 12.9 (13.0); S, 30.1 (29.7).

p-Toluyl; mp 82–84 °C; λ_{max} 232 and 290 nm in 20% ethanol in deoxygenated water. Anal. (calcd values for C₈H₁₂N₂S₂ in parentheses): C, 48.0 (48.1); H, 6.0 (6.0); N, 13.9 (13.9); S, 32.0 (31.9).

Alternatively, the aryldithiocarbamates were obtained in situ as sodium salts by adding a solution of 3 mmol of CS_2 in 2 mL of dioxane and 2.74 mmol of the corresponding aniline to 4.3 mL of 0.65 M NaOH (2.74 mmol) in a 10 mL Erlenmeyer flask, following the same procedure used for the ammonium salts.

Kinetics. Runs of UV spectra and kinetics measurements for the pH–rate profiles were followed at 290 nm, allowing the solution without the substrate to equilibrate thermically for 10 min, and using thermostated quartz cells at the set temperature ± 0.1 °C.

All runs gave first-order rate constants that were calculated using appropriate software, from the average of at least three runs with correlations no less than 0.99. The ionic strength of the runs at pH > 0 was kept constant at 1.0 by the addition of



Figure 1. pH-rate profile of the acid decomposition of phenyldithiocarbamate in 20% aqueous ethanol at 25 °C: continuous line, calculated rate constant; \bigcirc , sodium salt; \bullet , ammonium salt.

KCl. The kinetics were started by rapidly adding, with the aid of a Teflon plunger, 5 μ L of the sodium salt solution prepared in situ to a deoxygenated acidic solution of 20% v/v aqueous ethanol to avoid the oxidation of the dithiocarbamate to thiouram. The final concentration of the arylDTC was about 10⁻⁴ M. Similar values for the rate constants were obtained from the decomposition of the ammonium salts.

Activation Parameters. Activation parameters were calculated from the k_0 values in the range of 15.0–30.0 °C by least-squares fitting to the Eyring equation.

Kinetic Solvent Isotope Effect and Proton Inventory. Deuterium oxide, deuterated ethanol, ethanol, and distilled deionized water were all previously deoxygenated by boiling under nitrogen and then kept in sealed bottles. The % D was calculated for D₂O and EtOD by ¹H NMR using acetone as the internal standard. The kinetic solvent isotope effect and proton inventory were measured by mixing equal volumes of 20 v/v % EtOL in L₂O containing the substrate and 0.2 M L₂-SO₄ in 20% v/v EtOL in L₂O, in a stopped-flow spectrometer.

Results and Discussion

pH–**Rate Profiles.** The pH–rate profiles of the acid cleavage of arylDTCs show a dumbell shape (Figure 1) similar to that found for the alkylDTCs,⁵ where the observed first-order rate constant can be expressed by eq 2.

$$k_{\rm obs} = \frac{k_{\rm o}}{\frac{K_{\rm a}}{a_{\rm H^+}} + 1 + \frac{a_{\rm H^+}}{K^+}}$$
(2)

The acid dissociation constants of the dithiocarbamic acids (pK_a) and their conjugate acids (pK^+) were calculated from the pH-rate profiles (Scheme 1). The value of k_0 was obtained from the average value of k_{obs} at the plateau (Table 1). The value of k_0 represents the rate constant of the decomposition through the free dithiocarbamic acid (k_1 in Scheme 1) and is kinetically equivalent to $k_H K_a$, where k_H is the specific acid catalysis rate constant of the decomposition of the dithiocarbamate anion through the zwitterion **SH**[±]. Comparatively, for ArylDTCs, k_0 is about 10⁴-fold faster than alkDTCs from parent amines with $pK_N < 10.5$

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Table 1. Dissociation and Rate Constants Related to theAcid Cleavage of p-Substituted Aryldithiocarbamates in20% Aqueous Ethanol at 25 °C

p-XC₆H₄NHC(S)SH

х	p <i>K</i> _N ^a	pKa	р <i>К</i> +	k_{0}, s^{-1}	$10^{-2}k_{ m H}, M^{-1} { m s}^{-1k}$
MeO	5.29	3.0 ± 0.4	-2.7 ± 0.3	1.40 ± 0.14	14.0
Me	5.07	2.8 ± 0.04	-2.6 ± 0.05	2.14 ± 0.08	13.5
Н	4.58	2.7 ± 0.08	$-$ 3.1 \pm 0.04	2.80 ± 0.04	14.0
Cl	3.81	2.4 ± 0.02	$-~3.3\pm0.09$	3.06 ± 0.10	7.7
NO_2	0.98	1.7^{c}	-4.9^{c}	9.0 ^c	4.5^{d}

^{*a*} Handbook of Biochemistry; Sober, H. A., Hart, R. A., Eds.; CRC: Cleveland, 1968. ^{*b*} Calculated from $k_{\rm H} = k_0/K_{\rm a}$. ^{*c*} Extrapolated values. ^{*d*} From ref 1.



Figure 2. Dependence on the pK_N of the parent amine of the pK_a of dithiocarbamic acids: \bullet , this work; \bigcirc , alkylDTC, ref 5.



Figure 3. Dependence on the pK_N of the parent amine of the pK^+ of the conjugate dithiocarbamic acids: \bullet , this work; \bigcirc , alkylDTC, ref 5.

Acid Dissociation Constants of Aryldithiocarbamates. From the plots of pK_a (or pK^+) vs pK_N (Figures 2 and 3), it can be observed that the values for the arylDTCs are much higher than those for the alkDTCs with similar pK_N values, corresponding to basicities of an alkylic nitrogen of about 4.9 and 8.0 units of pK, respectively, higher than the pK_N of the parent anilines. The higher values might be due to the inhibition of the delocalization of the nitrogen electron pair into the benzene ring on account of the strong effect of the thiocarbonyl group that acts as a powerful electron sink.⁵



Figure 4. Brønsted plot of the rate constants and the pK_N of the leaving amine for the acid decomposition of substituted methyldithiocarbamates (\bigcirc , \Box) in water at 25 °C:^{5.6} k_2 and k_3 , as defined in Scheme 1; k_H , specific acid rate constant; \blacktriangle , k_H value for phenyldithiocarbamate; $\textcircled{\bullet}$, piperidinedithiocarbamate.¹

The conjugate acid presents total inhibition of resonance with the benzene ring, and consequently, 8 units of pK represents the maximum increase in basicity.

The same reason can be ascribed to the low pK_a values observed for the NH dissociation of some dithiocarbamic esters.⁸ The difference in pK_a between *N*-benzyl and *N*-phenyl esters is only 2.3 pK units, the same as the value obtained for the NH dissociation of the corresponding dithiocarbamic acids.⁹ The smaller value in comparison with the difference between benzylamine and aniline of 4.8 pK units supports the assumption that aryldithiocarbamates behave as derivatives of strong basic amines.

An increase in the basicity of the nitrogen by about 5-8 pK units places the arylDTCs in the pK_N range where a new mechanism of cleavage has been proposed to occur.⁵ In Figure 4, it can be observed that the specific acid rate constant k_H of phenylDTC corresponds to an alkDTC from a parent amine with a pK_N about 7 pK units higher than that of aniline.

A further piece of support for this theory was obtained from the Yukawa–Tsuno (Y–T) equation.¹⁰ This relationship combines linearly σ^{0} Hammett normal substitu-

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 Table 2.
 Activation Parameters of PhenylDTC and 2-Ammonium-EthylDTC

	р <i>К</i> _N	k_{0}, s^{-1}	ΔG , kcal/mol	ΔH , kcal/mol	ΔS , cal mol ⁻¹ K ⁻¹
PhenylDTC 2-Am-EtDTC	4.58 7.52	2.80 ± 0.04 a $(20.9 \pm 0.2) imes 10^{-4b}$	$\begin{array}{c} 16.80 \pm 0.01 \\ 21.16 \pm 0.05 \end{array}$	15.14 19.47	$\begin{array}{c} -5.6 \\ -5.7 \end{array}$

^a H₂SO₄ (0.1 M), $\mu = 1.0$ (KCl), and 20% v/v aqueous ethanol, 25 °C. ^b Water, 25 °C.⁵



Figure 5. Yukawa–Tsuno plot for the acid decomposition of aryldithiocarbamates in 20% v/v aqueous ethanol at 25 °C: \bigcirc , Brown σ^+ constant; \bullet , σ^0 Hammett constant; \Box , $\bar{\sigma}$ Y–T constant; $\rho = 0.68$, $r^+ = 0.27$. For H and *p*-NO₂, σ^+ and σ^0 are the same.

ent constants, which do not involve π -electronic interactions between the substituent and the reaction center, and Brown σ^+ constants, where a positive charge can be delocalized into a π -arylic system. The substituent effects can be more generally described by the Y–T equation in the form

$$\log \frac{k}{k_0} = \rho \bar{\sigma} = \rho (\sigma^0 + r^+ \Delta \bar{\sigma}^+)$$
(3)

where $\Delta \bar{\sigma}^+ = \sigma^+ - \sigma^0$ measures the capability for π -delocalization of π -electron donor substituents, and r^+ is a constant characteristic of a reaction and measures the extent of resonance interaction between the aryl group and the reaction center in the rate-determining transition state. For $r^+ = 1$, the resonance effect predominates, while when $r^+ = 0$, the effect does not involve π -electronic interaction. The Yukawa–Tsuno plot for the arylDTC series (Figure 5) showed $\rho = 0.68$; that is, the reaction presents very low sensitivity for *p*-substituents, and because the low value of $r^+ = 0.27$, the effect is predominantly inductive rather than resonant.

Activation Parameters. In Table 2, a comparison is made between the activation parameters of phenylDTC and 2-ammonium-ethylDTC. Despite the fact that the pK_N of the first is about 3 pK units lower, k_0 is about 3 orders of magnitude faster. The increase in reactivity is mainly due to a decrease in the enthalpy of activation. For alkylDTCs with $pK_N < 9.2$, the slowest step is the N-protonation of the dithiocarbamate anion that forms a zwitterion followed by a fast C–N bond cleavage (Scheme 1, Figure 4).⁵ At $pK_N > 10.5$, a minimum of the Br ϕ nsted plot indicates a change of mechanism.^{11,12} The fast increase in the rate constant at higher pK_N is

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Kinetic Solvent Isotope Effect and Proton Inventory. Inverse solvent isotope effect for acid catalysis is consistent with a partial transfer of the proton at a late transition state of the rate-determining step. The pHindependent rate constant k_0 of phenylDTC exhibits an inverse SIE $k_0^D/k_0^H = 2.51$. If the aryldithiocarbamates behave as derivatives of strong basic amines and decompose through an intramolecular S to N proton-transfer mechanism, proton inventory could give insight into the structure of the transition state involved.

For phenylDTC, the k_n vs *n* plot was bulged downward, which always indicates the existence of a multiproton transition state (Table 3, Figure 6).^{13,14} Consistently, the plot of ln k_n vs *n* was linear (r = 0.998) and $k_{0.5} = (k_0 k_1)^{1/2}$ = 4.44 was very similar to the experimental value of 4.34. However, there must be more than two protons undergoing change upon activation because the plot of $(k_n/k_0)^{1/2}$ vs *n* was not linear and $(k_1/k_0)^{1/2} = 1.59$ is too high for the fractionation factor of the transition state (assuming that each proton contributes the same isotope effect). This analysis suggests that the S to N transfer occurs through a water molecule as shown in eq 4. Preliminary theoretical calculations carried out at the HF/3-21 G(d) level support this assumption because it was found that for phenvldithiocarbamate, the water-catalyzed mechanism is strongly favored with respect to the direct intramolecular proton transfer by 13 kcal/mol.¹⁵ According to this mechanism, the Gross-Butler equation has the form of eq 5.



$$k_{n} = k_{0} \left(\frac{(1 - n + n\phi_{N-L}^{T_{1}})}{(1 - n + n\phi_{NL})} \right)_{sec} \left(\frac{(1 - n + n\phi_{O-L}^{T_{2}})}{(1 - n + n\phi_{O-L})} \right)_{sec} \left(\frac{(1 - n + n\phi_{S-L-O}^{T_{3}})(1 - n + n\phi_{O-L-N})}{(1 - n + n\phi_{S-L})(1 - n + n\phi_{O-L})} \right)_{pri}$$
(5)

There are two hydrogens (N–L and O–L) experiencing some change in bonding, contributing as a secondary SIE, and two protons (S–L–O and O–L–N) being transferred at the transition state, contributing as a primary SIE.

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Table 3. Proton Inventory of the Acid Decomposition of Ammonium Phenyldithiocarbamate at 25.0 °C^a

X _D	$k_{\rm n}^{\rm exp}$, s ⁻¹	$(RSC)^b$	$(k_{\rm n}/k_{\rm o})_{\rm sec}^{{ m N-L}c}$	$k_{\rm n}^{\rm calcd}$, s ^{-1d}
1.00	$(7.04)^{e}$	0.40	1.049	7.34
0.94 ± 0.01	6.62 ± 0.04	0.436	1.046	6.72
0.85 ± 0.01	6.06 ± 0.02	0.490	1.041	5.95
0.66 ± 0.01	5.13 ± 0.04	0.604	1.031	4.78
0.47 ± 0.01	4.08 ± 0.03	0.718	1.022	3.98
0.28 ± 0.00	3.56 ± 0.02	0.832	1.013	3.41
0.09 ± 0.00	2.90 ± 0.03	0.946	1.004	2.97
0.0	2.80 ± 0.04	1.000	1.000	2.80

^{*a*} In L₂SO₄ 0.1 M and 20% v/v aqueous EtOL. ^{*b*} (RSC) = (1 - n)+ $n\phi_{S-L}$); $\phi_{S-L} = 0.40$. ^c From eq 6; $\phi_{N-L} = 0.92$; $\phi_{N+-L} = 0.97$; $\chi = 0.9$. ^d From eq 7; (TSC) = 1. ^e Extrapolated.

A late transition state would look very similar to a zwitterion, where the S to O and O to N transfers are almost complete. The charge on the oxygen of the water molecule would be very small, and consequently, the secondary effect due to the O-L bond would be very close to unity. The secondary effect due to the N-L bond was estimated from eq 6 where χ is the weighting factor describing the TS structure.

$$\left(\frac{k_{\rm n}}{k_{\rm o}}\right)_{\rm sec}^{\rm N-L} = \left(\frac{(1-n+n\phi_{\rm N^+-L})}{(1-n+n\phi_{\rm N-L})}\right)_{\rm sec}^{\chi} \tag{6}$$

Since it is a late TS, the calculation of this effect was made for $\chi = 0.9$. This value seems reasonable because the calculated value was only 0.4% lower than the equilibrium value ($\chi = 1$) for n = 1.

Therefore, eq 5 can be simplified as eq 7 where (TSC) and (RSC) are the

$$k_{\rm n} = k_{\rm o} \left(\frac{k_{\rm n}}{k_{\rm o}}\right)_{\rm sec}^{\rm N-L} \left(\frac{\rm TSC}{\rm RSC}\right) \tag{7}$$

TS and reagent state contributions to the primary SIE, respectively, given by eq 8 (considering that $\phi_{O-L} = 1.0$).

$$(TSC) = (1 - n + n\phi_{S-L-O}^{T_3})(1 - n + n\phi_{O-L-N}^{T_4})$$
(8a)

$$(RSC) = (1 - n + n\phi_{S-I})$$
 (8b)

Calculation of TSC, considering the SIE from N-L secondary isotope effects, gave an average value of 1.02 \pm 0.03.

The maximum equilibrium value (MEV) for the cleavage of the dithiocarbamic acid by concerted intramolecular N-protonation and C–N bond breakdown (SH \leftrightarrow N in Scheme 1) is only 2.30. However, when considering a slow intramolecular N-protonation to form a zwitterion $(SH \leftrightarrow SH^{\pm})$, followed by fast C–N bond cleavage, the MEV increases to 2.56. This value is very reasonable when compared to the observed value of 2.51.

The mechanism could also be concerted: an asynchronic process where the N-protonation is more advanced than the C-N bond breakdown. Nonetheless, this mechanism implies an intramolecular general acid catalysis by an acid of low pK_a value (2.7), which has been shown to be incapable of acting as an effective intramolecular catalyst.6 Therefore, the structure of the TS should explain why the intramolecular N-protonation occurs so easily and the C-N bond breaks so fast for a species whose N-basicity corresponds to a pK_N higher than 10 (Figure 4).





Figure 6. Proton inventory of the acid decomposition of ammonium phenyldithiocarbamate at 25.0 °C in L₂SO₄ 0.1 M and 20% v/v aqueous EtOL. Continuous curve was drawn according to eq 5, where $\phi_{O-L} = 1.0$, $\phi_{S-L} = 0.40$, $\phi_{N-L} = 0.92$; $\phi_{\rm O-L}^{\rm T}$ = 1.0, $\phi_{\rm N^4-L}^{\rm T}$ = 0.97.

Water Catalysis. Water acts as an acid-base catalyst, but the main effect is that in order to reach the transition state, a torsion is imposed on the C-N bond that decreases its double-bond character and has a weakening effect. As observed in Table 1, electron-withdrawing groups accelerate the decomposition because they decrease the partial C-N double bond. The extent of the torsional angle θ (I)



is also related to the decrease in resonance of the aromatic ring and the nitrogen, increasing its basicity.

Several examples in the literature show the doublebond character and rotational hindrance around the C-N bond for amides and thioamides $^{\rm 16}$ and thiocarbamic esters.^{17,18} In normal amides, the carbonyl group becomes deactivated by the resonance of the N-lone pair with the C=O group. However, for acylimidazols, the charges on N-1 and N-3 show that the electron pair is pulled in the opposite direction,¹⁹ activating the carbonyl and increasing the reactivity of these compounds (II and III).²⁰

This is similar to the effect observed in the aryldithiocarbamates, where the electron pair is shifted from the

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nitrogen to the thiocarbonyl group, thus decreasing the resonance with the benzene ring.

The high double-bond character of the C-N bond in N,N-dialkylthioamides prevents the free rotation^{16,17} with a rotational barrier in the range of 20-23 kcal/mol.²¹ This barrier is near the activation barrier of the arylDTCs and suggests that the driving force to reach the transition state is the needed torsion of the C-N bond that inhibits the resonance with the thiocarbonyl group and the aromatic moiety, increasing the basicity of the nitrogen and making the proton transfer thermodynamically favorable. The increase in basicity must be assisted by the lack of coplanarity of the benzene ring and the dithiocarbamic group.

Amide Group. There is a relationship between these results and certain properties of the amide group that is particularly relevant to the chemistry of peptides and proteins and the reactions involved in their transformations, especially those that are catalyzed by enzymes. It has been suggested that an important feature of the action of the peptidase enzyme might be the twisting effect on the amide moiety as it binds to the active site, restricting the resonance and enhancing the ease of C-N bond breakage.22

The conjugation of the nitrogen lone-pair is optimum when the CO-N unit is planar, leading to the partial double-bond character of the C-N bond that hinders the internal rotation at the same time that it weakens the C=O bond, lowering the carbonyl stretching frequency. Recently, Kirby et al.²³ have shown that there is a linear correlation between the ionization potential IP[n(O)]related to the oxygen lone-pair orbital n(O) and the frequency that was corrected for angle strain v_{120} (C=O) of the carbonyl vibration. Compounds with a twisted

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amide bond diverge from this linear correlation. Thus, 3,5,7-trimethyl-1-azaadamantan-2-one, which is the most twisted amide (the N-electron lone-pair is coplanar with the C=O group), presents a strong inhibition of the *n*(N)- $\pi^*(C=O)$ interaction that significantly stabilizes n(O). The value of IP[*n*(O)] falls well off of the straight line, and 3,5,7-trimethyl-1-azaadamantan-2-one is better described as an aminoketone than as an amide. There is very little decrease in the bond length of the C=O group with distortion, but the increase in the CO-N bond proves to be substantial, indicating that inhibition of the amide resonance leads to a normal C-N single bond length. For the arylDTCs, twisting the CS-N bond at the transition state involves the pyramidalization of the amino group and possibly the thiocarbonyl carbon atom. The overall distortion is measured by the angular parameter θ (I).

Conclusions

The spontaneous acid decomposition of aryldithiocarbamates is more than 104-fold faster than that of alkyldithiocarbamates with similar pK_N values. The reaction is catalyzed by a water molecule that acts as an acidbase catalyst. The mechanism could be a slow intramolecular N-protonation to form a zwitterion, followed by fast C-N bond cleavage, or concerted where, at the TS, the N-protonation is more advanced than the C-N bond breakdown. The main driving force to reach the TS is the torsional effect on the C-N bond that inhibits the resonance with the thiocarbonyl group.

Acknowledgment. This work was written in part during the stay of E.H. at the Institute of Fundamental Research of Organic Chemistry at Kyushu University, as Visiting Professor. E.H. thanks Dr. Shinjiro Kobayashi for the invitation. We also thank Profs. Cesar Zucco and Omar El Seoud for allowing us to use their stopped-flow spectrometers for some of the kinetics measurements.

JO016190T

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