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THE THERMAL REARRANGEMENT OF THIONOCARBAMATES TO THIOLCARBAMATES

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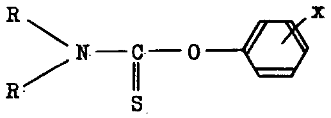
The thermal rearrangement of thionocarbamates of the formula $R_2N\text{-}C(=S)\text{-}O\text{-}Ar$ (I) into thiolcarbamates of the formula $R_2N\text{-}C(=O)\text{-}S\text{-}Ar$ (II) has recently been reported.$^{1,2)}$ This paper describes the kinetics of the rearrangement in order to elucidate the reaction mechanism.
The kinetic experiments were run by keeping the compounds (I), in Table I, at 170° or 190° without any solvent and followed by measuring the amount of the products (II) by ultraviolet spectrophotometry. The data thus obtained showed that the reactions were strictly first-order.
The products (II) obtained are shown in Table II. The change of the rate constants (k), in Table I, indicated that the rearrangement was favoured by an electron-withdrawing group in the benzene ring. Ordinary Hammett plots of log k vs. σ (σ^-) did not give a linear relationship (Fig. 1). By assuming that r = 1.60 in Yukawa-Tsuno equation,$^{3)}$ however, the plots between log k and $\sigma^0 + r\Delta\bar{\sigma}_R^-$ gave a good straight line with $\rho = +1.92$ (Fig. 2). A large positive r-value suggests that a transition state is greatly stabilized by an additional resonance effect caused by the para substituents.

With a series of 4-nitrophenyl N,N-dialkylthionocarbamates (I-11 to I-14), the influence of the alkyl group, R, on the reaction rate was

TABLE I. ARYL N,N-DIALKYLTHIONOCARBAMATES

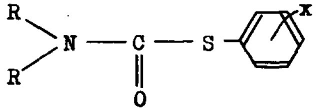


Compd. No.	R	x	σ	M.p. °C	k x 10^2 min^{-1} at 190°C	170°C
I- 1	CH_3	4-CH_3	-0.170	94 - 95	——[g]	——
I- 2	CH_3	H	0	29.5-30	——[g]	——
I- 3	CH_3	4-Cl	+0.227	58 - 59	0.07	——
I- 4	CH_3	3-Cl	+0.373	90.5-91.5	0.07	——
I- 5	CH_3	3-CF_3	+0.43	64 - 65[c]	0.09	——
I- 6	CH_3	4-CO_2Et	+0.45 (+0.68)[a]	81.5-82.5	0.54	——
I- 7	CH_3	4-$COCH_3$	+0.502 (+0.87)[a]	101.5-102.5[d]	1.24	——
I- 8	CH_3	4-CN	+0.660 (+1.00)[a]	116-117	2.67	——
I- 9	CH_3	3-NO_2	+0.710	147-148[e]	0.32	——
I-10	CH_3	4-SO_2CH_3	+0.72 (+1.05)[a]	181-182	2.71	——
I-11	CH_3	4-NO_2	+0.778 (+1.27)[a]	146.5-147.5[f]	18.12	4.44
I-12	C_2H_5	4-NO_2	-0.100[b]	93.5-94.5	——	7.47
I-13	n-C_3H_7	4-NO_2	-0.115[b]	96.5-97.5	——	7.71
I-14	i-C_4H_9	4-NO_2	-0.125[b]	80 - 81	——	9.41
I-15	C_2H_5	4-CN	——	75 - 76	——	——

a) The values in parenthese are σ^-. b) σ^* value for R.

c)~f) lit. 2). g) These compounds did not rearrange even at 190°C, 30 min.

TABLE II. ARYL N,N-DIALKYLTHIOLCARBAMATES



Compd. No.	R	x	M.p. °C
II- 1	CH_3	4-CH_3	36 - 37[a)]
II- 2	CH_3	H	43 - 44[a)]
II- 3	CH_3	4-Cl	80.5-81
II- 4	CH_3	3-Cl	46-47.5
II- 5	CH_3	3-CF_3	31 - 32[b)]
II- 6	CH_3	4-CO_2Et	55-56.5
II- 7	CH_3	4-$COCH_3$	107-108[c)]
II- 8	CH_3	4-CN	103-104
II- 9	CH_3	3-NO_2	120-121[d)]
II-10	CH_3	4-SO_2CH_3	154-155.5
II-11	CH_3	4-NO_2	121-122[e)]
II-12	C_2H_5	4-NO_2	48 - 49
II-13	n-C_3H_7	4-NO_2	175/0.4[f)]
II-14	i-C_4H_9	4-NO_2	183/0.2[f)]
II-15	C_2H_5	4-CN	59.5-60.5

a) Prepared by the reaction of N,N-dimethylcarbamoyl chloride with corresponding thiol. b)~e) lit. 2). f) B.p. °C/mm.

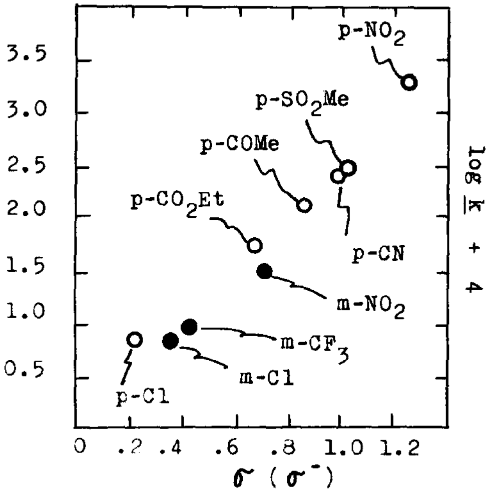


Fig. 1 Plots of log $\underline{k}$(190°) $\underline{vs}$. σ (σ^-)

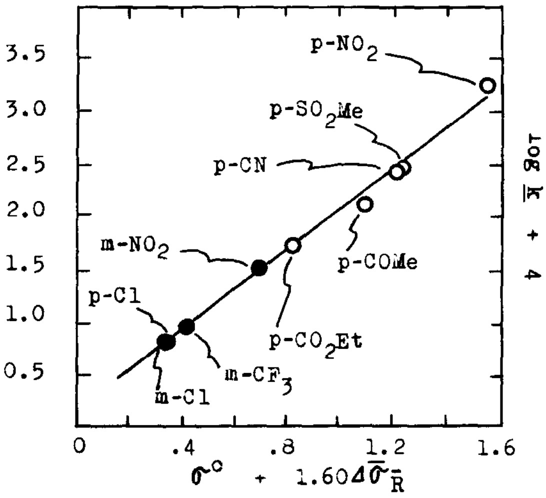


Fig. 2 Plots of log $\underline{k}$(190°) $\underline{vs}$. ($\sigma^0 + 1.60\Delta\bar{\sigma}_{R}$)

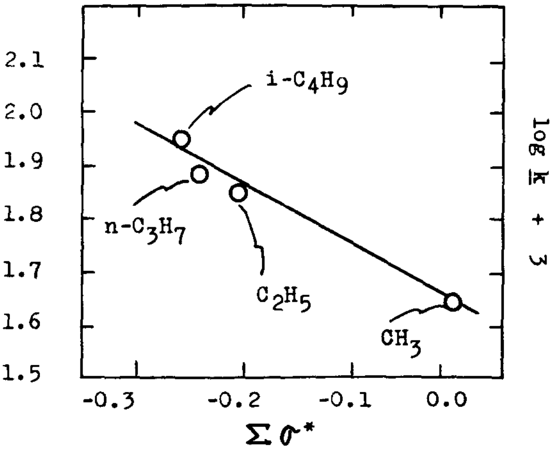
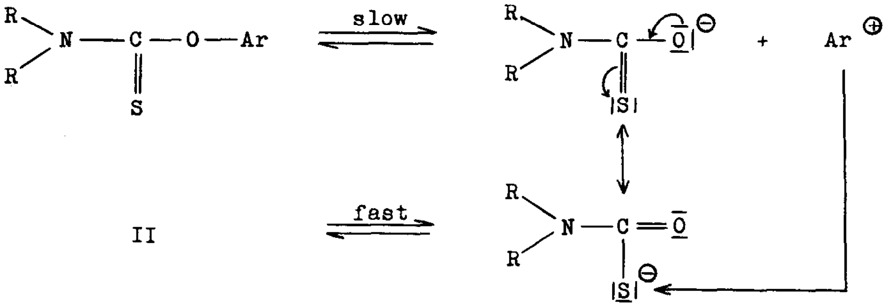


Fig. 3 Plots of log $\underline{k}$(170°) $\underline{vs}$. $\Sigma\sigma^*$ for a series of $R_2N\text{-}C(=S)\text{-}O\text{-}C_6H_4\text{-}NO_2(p)$

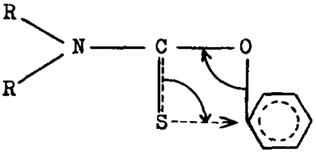
investigated. The data are contained in Table I. Since the plots between log <u>k</u> and Taft's σ^*,4) concernig the above four compounds, gave a good straight line with ρ^* = +1.09 (Fig. 3), the steric bulkiness of R seems to have no significant influence on the reaction rate.

Two kinds of the crossover reactions with two pairs of the compounds (I) (I-11 with I-15 and I-8 with I-12) were tested to determine whether the reaction is SN$_1$-like such as Scheme 1 or intramolecular,



Scheme 1

but both the crossover reactions gave no crossover products. These results show that the rearrangement proceeds through an intramolecular mechanism. The mechanism can be well explained by assuming a four-membered cyclic system at the transition state caused by a nucleophilic attack of the sulphur atom to the carbon atom of position 1 in the benzene ring as shown in Scheme 2.



Scheme 2

Since the stronger electron-donating inductive effect of R may promote the nucleophilic character of the sulphur atom, the rearrangement rate of $R_2N\text{-}C(=S)\text{-}O\text{-}C_6H_4\text{-}NO_2(p)$ (I-11 to I-14) should increase in the order of R = $i\text{-}C_4H_9 > n\text{-}C_3H_7 > C_2H_5 > CH_3$. This expectation is in accord with the results in Fig. 3.

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REFERENCES

1) Presented in part at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965 (Journal of the Meeting, p. 175, No. 9505, **1965**).
2) M. S. Newman and H. A. Karnes, J. Org. Chem., **31**, 3980 (1966).
3) Y. Yukawa and Y. Tsuno, Bull. Chem. Soc. Japan, **37**, 971 (1959): Y. Yukawa, Y. Tsuno and M. Sawada, ibid., **39**, 2274 (1966).
4) M. S. Newman, ``Steric Effects in Organic Chemistry'', Wiley, New York (1956) p. 619.