Table V

Reactions of 1,1′,2,2′-Tetrabutoxyethane[a]

Reactants	Unreacted acetal	1,3-Dioxolane (dimer)	Bis-dioxolane (trimer)	Butanol
	Products yield,[b] %			
Water	38.8	37.0	5.4	26.4
Aqueous glyoxal	6.6	51.7	34.4	22.0

[a] The stoichiometry of the reaction with glyoxal was 1:1. The water reaction was run with the same water stoichiometry as was present in the reaction with glyoxal. [b] No free glyoxal was observed in these reaction mixtures.

in water, described by Whipple, is further complicated by an equilibrium between the water layer and water-insoluble alcohol, one might expect to see a wide range of yields of products. For example, if only tetrahydroxyethane goes into the hexanol layer the result would be (1) the formation of more acetal based on glyoxal monomer and (2) a decrease in the amount of dimer present in the aqueous phase. Another explanation might lie in the relative rates of acetal formation and exchange of the various species in the glyoxal solution.

Support for the above consideration of the complex equilibria of glyoxal in water comes from those experiments in which the concentration of glyoxal was varied as well as the molar ratio of alcohol to glyoxal (Table IV).

This table (IV) clearly shows that the change in equilibrium in going from 40 to 80% glyoxal provides higher yields of dimeric, trimeric, and even higher products. Even more striking is the reaction in which only half as much alcohol is present per mole of tetrahydroxyethane (hydrated glyoxal). It is in that case that we see the largest yield of dimer and trimer product.

The equilibrium reactions in Scheme I represent the two most probable mechanistic pathways to our observed products in which pathway B represents the glyoxal equilibria to products, and pathway A proposes the direct insertion reaction of glyoxal with acetals.

Support for the above pathways and equilibria was obtained by a study of the reactions of 1,1′,2,2′-tetrabutoxyethane with water and with aqueous glyoxal. The results of those reactions are given in Table V.

The reaction of 1,1′,2,2′-tetrabutoxyethane with water gives a 61% conversion of acetal whereas with glyoxal the conversion was 94%. In both cases the butanol yield indicates the same degree of hydrolysis reaction took place; so the only difference must be in the availability and concentration of glyoxal for direct insertion. This conclusion is augmented by the relatively unchanged yield of dimeric product and the six- to sevenfold increase in trimeric product.

We conclude from this study that this direct insertion reaction is a viable pathway and, indeed, plays a part in controlling the product mixture in the multiphase reactions described earlier.

The formation of glycolates in these reactions will not be discussed in this report, but will be taken up in a future publication.

Registry No.—**1**, 37160-54-6; **2**, 37160-55-7; **3**, 37160-56-8; **4**, 37160-57-9; **5**, 37160-58-0; **6**, 37160-59-1; **7**, 37160-60-4; **8**, 37406-80-7; **9**, 37160-61-5; **10**, 37160-62-6; **11**, 37160-63-7; **12**, 4704-23-8; **13**, 16646-44-9; **14**, 37160-66-0; **16**, 7397-62-8; **17**, 6284-81-7; **18**, 37160-68-2; **19**, 37160-69-3; **20**, 3975-14-2; **21**, 37160-71-7; **22**, 96-35-5; **23**, 2517-44-4; **24**, 33834-49-8; **25**, 33834-90-1; **26**, 37160-75-1; **27**, 37160-76-2; glyoxal, 107-22-2.

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Inductive Effect in Dithiocarbamate Decomposition Mechanism

D. De Filippo,* P. Deplano, F. Devillanova, E. F. Trogu, and G. Verani

Istituto Chimico Policattedra, Università di Cagliari, Cagliari, Italy

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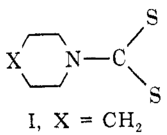
The acid-induced decomposition of $X(C_2H_4)_2NCS_2^-$ ions (X = CH_2, O, S, HN, CH_3N) was spectrophotometrically studied in pseudo-first-order conditions by varying ionic strength, dielectric constant, pH, and temperature. The reaction is first order with respect to the H^+ and dithiocarbamate ions. Activation parameters and activated complex radius values are also reported.

Some authors[1-6] have studied the dithiocarbamate ion decomposition mechanism using polarographic, potentiometric, or spectrophotometric techniques. Although some aspects of the problem have been clarified, we believe that this subject has not been completely dissected. In fact, ionic strength and the type of acid catalysis have never been considered, and the influence of dielectric constant variation has not been well defined. Moreover, increases of even 100-fold in decomposition rate constants have been explained by referring to steric and sometimes to electronic factors. In this paper we intend to carry out a more detailed treatment using a homogeneous series of ions, where it is possible to point out the inductive effects, such as shown below.



I, X = CH_2
II, X = O
III, X = S
IV, X = NH
V, X = CH_3N

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(1) H. Bode, *Z. Anal. Chem.*, **142**, 414 (1952).
(2) P. Zuman and R. Zahradnik, *Z. Phys. Chem.*, **208**, 135 (1958).
(3) R. Zahradnik and P. Zuman, *Collect. Czech. Chem. Commun.*, **24**, 1132 (1959).
(4) D. M. Miller and R. A. Latimer, *Can. J. Chem.*, **40**, 246 (1962).
(5) S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *Anal. Chem.*, **41**, 1441 (1969).
(6) S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *J. Phys. Chem.*, **74**, 860 (1970).

Results

Kinetics were studied by spectrophotometric measurements; the maxima wavelengths and ϵ values are reported in Table I. The maxima near 260 nm and near 350 nm have been attributed by many authors[7-12] to the transition $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively, while the intense band around 280 nm, which is present in dithiocarbamate only, was tentatively assigned to an $n \rightarrow \sigma^*$ transition[13] on the basis of solvent effect and by comparison with the diselenocarbamic derivatives spectra.

TABLE I

UV MAXIMA WAVELENGTHS, MOLAR ABSORBANCE VALUES IN ALKALINE AQUEOUS SOLUTION, AND ASSIGNMENTS

	$\pi \rightarrow \pi^*$		$n \rightarrow \sigma^*$		$n \rightarrow \pi^*$	
Compd	nm	ϵ	nm	ϵ	nm	ϵ
I	261	15,800 ± 200	280	15,800 ± 100	346	68
II	262	16,100 ± 200	286	16,800 ± 100	341	122
III	261	15,200 ± 80	286	17,050 ± 70	349	63
IV	269 sh	24,500 ± 300	283	22,400 ± 200	350	88
V	261	17,400 ± 400	285	17,000 ± 300	347	101

The decomposition stoichiometry for I, II, and III, potentiometrically verified, is of the type shown in eq 1,

$$X(C_2H_4)_2NCS_2^- + 2H^+ \longrightarrow X(C_2H_4)_2NH_2^+ + CS_2 \qquad (1)$$

whereas in the case of IV and V one H^+ ion more is consumed, including the X-substituent protonation.[14]

Each run was conducted under *pseudo-first-order* conditions, *i.e.*, at $[H^+]$ constant, with the use of the proper buffer solution (acetic acid–acetate). Therefore in every table the reported k values are first order with respect to the dithiocarbamate ion.

Working at 25° and with buffered ionic strength gave the result that in the explored range (pH 4.32–6.41) the reaction is of the first order with respect to H^+ ion (Table II).

Activation parameters were determined[15,16] (Table III) by varying the temperature (from 15 to 40°) and keeping pH (5.92) and ionic strength (1.00) values constant.

The influence of ionic strength, studied in the range 0.005–1.00, on the rate-constant value, determined at pH 5.00 and 25° (see Table IV), is, on the whole, moderate. Nevertheless, the shape of the graphs log k *vs.* $\mu^{1/2}$ (Figure 1) is noteworthy because a maximum is present for all compounds. This behavior was also confirmed for II and IV at pH 5.88.

With another set of measurements we found that the log k values are linear *vs.* $1/D$ (for water–methanol mixtures: MeOH wt % 0–76), keeping constant μ 0.1, $T = 25°$, and the molar ratio ($[A^-]/[HA] = 1.745$) of the buffer solution (Table V).

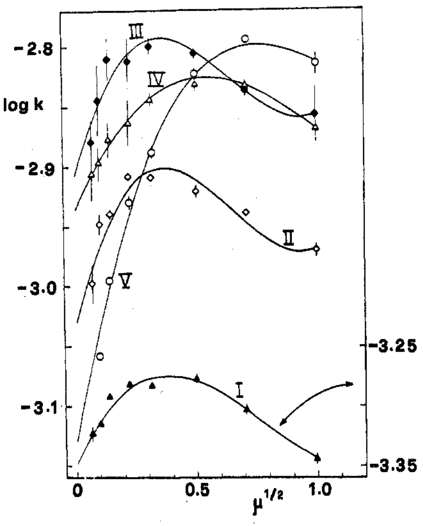

Figure 1.—Influence of ionic strength on the rate constant for the decomposition $X(C_2H_4)_2NCS_2^-$ ions, where X = (I) CH_2; (II) O; (III) S; (IV) NH; (V) CH_3N.

In order to check whether the reaction is subject to general acid or specific hydrogen ion catalysis, some experiments were carried out in the presence of various buffer solutions (formic, acetic, and propionic acids and their sodium salts).

Results and Discussion

First we observe that (1) the reaction shows a total order of two [one with respect to H^+ and one with respect to dithiocarbamate (DTC^-) ions]; (2) the wavelengths of the maxima, characteristic of DTC^-, do not move during the whole decomposition; (3) the maxima of DTCH, which would fall at lower wavelengths, do not appear, up to pH ≥4.3; (4) the absorbance of the reaction products (Am, AmH^+, AmH_2^{2+}) was seen to be negligible in the experimental range (240–310 nm).

Therefore in the proposed reaction scheme (eq 2) we

$$DTC^- + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} DTCH \xrightarrow{k_3} Am + CS_2 \xrightarrow{H^+} AmH^+ \underset{IV,V}{\overset{H^+}{\longrightarrow}} AmH_2^{2+} \qquad (2)$$

suggest that the DTCH species should be considered in a steady-state condition. Hence the observed rate constant is defined by eq 3, which, assuming that $k_2 \gg k_3$, could be simplified as follows: $k_{obsd} = k_3/K_a$.

$$k_{obsd} = \frac{k_3 k_1}{k_2 + k_3} \qquad (3)$$

On the other hand, recent polarographic studies[5] have demonstrated that the first protonation of DTC^- species occurs on the sulfur atom.

Furthermore, this reaction is subject to general acid catalysis, as demonstrated by a set of runs with compound I in different acid–base couples. The catalytic constants, k_c, were estimated by plotting k against [HA] values while the Brønsted coefficient (α 0.75 ± 0.05) was obtained from the straight line log k_c *vs.* log K_{HA}.

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(13) M. L. Shankaranarayana, *Acta Chem. Scand.*, **19**, 1113 (1965); **24**, 2065 (1970), and references cited therein.

(14) Because of the high rate constant values we found it impossible to follow the reaction course by measurements of the H^+ uptake required to keep the pH constant.

(15) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, p 199.

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, p 100.

TABLE II

VARIATION OF FIRST-ORDER OBSERVED RATE CONSTANTS, $k \times 10^4$ SEC^{-1}[a]

pH	I	II	III	IV	V
6.41	0.207 ± 0.001	0.500 ± 0.002	0.575 ± 0.000	0.672 ± 0.000	0.476 ± 0.000
5.85	0.744 ± 0.002	1.81 ± 0.03	2.19 ± 0.03	2.173 ± 0.0005	1.789 ± 0.004
5.36	2.246 ± 0.007	5.44 ± 0.08	7.01 ± 0.02	6.6 ± 0.3	5.64 ± 0.01
4.85	6.667 ± 0.002	16.9 ± 0.4	21.08 ± 0.04	18.5 ± 0.5	17.18 ± 0.05
4.32	23.18 ± 0.04	57.6 ± 1	71 ± 1	65 ± 3	56.7 ± 0.7
	0.97 ± 0.01	0.99 ± 0.01	1.00 ± 0.01	0.94 ± 0.01	1.00 ± 0.01

[a] Against pH at 25 ± 0.02° and μ 0.1 (acetic acid–acetate aqueous buffer solution). In the last line slope values of the equation $\log k = a - b\text{pH}$ are reported. Each value is the average of two to four.

TABLE III

FIRST-ORDER OBSERVED RATE CONSTANTS, $k \times 10^4$ SEC^{-1}[c]

Temp, °C	I	II	III	IV	V
15 ± 0.02	0.216 ± 0.0005	0.55 ± 0.01	0.686 ± 0.003	0.670 ± 0.000	0.899 ± 0.003
20	0.366 ± 0.002	0.93 ± 0.01	1.154 ± 0.002	1.106 ± 0.000	1.434 ± 0.005
25	0.629 ± 0.002	1.53 ± 0.05	1.922 ± 0.004	1.80 ± 0.04	2.351 ± 0.004
30	1.029 ± 0.0005	2.29 ± 0.05	2.90 ± 0.03	2.82 ± 0.04	3.48 ± 0.02
35	1.775 ± 0.0005	3.6 ± 0.1	4.88 ± 0.03	4.49 ± 0.05	5.42 ± 0.03
40	2.905 ± 0.006	5.5 ± 0.2	7.58 ± 0.09	7.1 ± 0.2	8.11 ± 0.03
E_a, kcal/mol	18.7 ± 0.2	16.4 ± 0.2	17.2 ± 0.2	16.9 ± 0.1	15.7 ± 0.2
$\Delta S^{\ddagger}$,[a] eu	−17.1 ± 0.6	−23.1 ± 0.9	−19.9 ± 0.7	−21.0 ± 0.3	−24.6 ± 0.6
$\Delta H^{\ddagger}$,[b] kcal/mol	18.1 ± 0.2	15.8 ± 0.2	16.6 ± 0.2	16.3 ± 0.1	15.1 ± 0.2

[a] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Process," McGraw-Hill, New York, N. Y., 1941, p 199, eq 175. [b] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1958, p 100, eq 51. [c] Ionic strength μ 1.00; pH 5.92 ± 0.04 (acetic acid–acetate buffer); each value is the average of four runs.

TABLE IV

VARIATION OF FIRST-ORDER OBSERVED RATE CONSTANTS, $k \times 10^4$ SEC^{-1}[a]

μ	I	II	III	IV	V
1.000	4.55 ± 0.08	10.7 ± 0.1	13.9 ± 0.8	13.6 ± 0.2	15.4 ± 0.3
0.500	4.98 ± 0.03	11.3 ± 0.2	14.6 ± 0.2	14.7 ± 0.2	16.10 ± 0.06
0.250	5.28 ± 0.04	12.0 ± 0.2	15.7 ± 0.1	15.07 ± 0.01	14.7 ± 0.1
0.100	5.21 ± 0.02	12.35 ± 0.02	15.9 ± 0.2	14.34 ± 0.00	13.0 ± 0.1
0.050	5.22 ± 0.04	12.39 ± 0.00	15.5 ± 0.6	13.7 ± 0.6	11.8 ± 0.2
0.020	5.12 ± 0.02	11.5 ± 0.3	15.5 ± 0.6	13.3 ± 0.4	10.10 ± 0.05
0.010	4.83 ± 0.03	11.53 ± 0.00	14 ± 1	12.6 ± 0.4	8.8 ± 0.3
0.005	4.76 ± 0.05	10.0 ± 0.3	12.9 ± 0.9	12.4 ± 0.6	8.69 ± 0.01
k_0	4.49 ± 0.09	12.3 ± 0.5	12.4 ± 0.6	11.6 ± 0.2	7.6 ± 0.2

[a] Against ionic strength, pH 5.00 ± 0.02 (acetic acid–acetate buffer); temperature 25 ± 0.02°. Each value is the average of two to four runs. In the last line the values of k_0 obtained from the empirical equation $\log k = \log k_0 + a\mu^{1/2} + b\mu + c\mu^{3/2}$ are reported.

TABLE V

VARIATION OF FIRST-ORDER OBSERVED RATE CONSTANT, $k \times 10^4$ SEC^{-1}

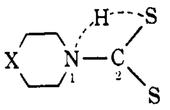
$1/D$	I	II	III	IV	V
2.266×10^{-2}	77 ± 5	50.3 ± 0.7	65 ± 0.2	39.6 ± 0.1	23.4 ± 0.8
2.032	51.8 ± 0.9	40 ± 3	54.8 ± 0.1	35.28 ± 0.00	17.5 ± 0.5
1.850	37.7 ± 0.7	35 ± 1	50 ± 2	30.04 ± 0.05	16.23 ± 0.5
1.704					16.0 ± 0.9
1.585	19.2 ± 0.3	26.0 ± 0.7	35.6 ± 0.4	23 ± 3	15.4 ± 0.4
1.486	14.1 ± 0.2				
1.402	10.4 ± 0.1	20.7 ± 0.8	28.2 ± 0.2	24 ± 3	16.7 ± 0.3
1.330	9.77 ± 0.2				
1.274	6.67 ± 0.00	16.86 ± 0.04	21.07 ± 0.04		8.74 ± 0.03
$r^{\ddagger}$ (Å)[a]	2.43	5.17	5.07	6.78	5.82

[a] C. H. Banford and C. F. H. Tipper, "Comprehensive Chemical Kinetics," Vol. II, "The Theory of Kinetics," Elsevier, Amsterdam, 1969. [b] Against dielectric constants (water–methanol mixtures) at 25 ± 0.02° and μ 0.01. The molar ratio in acetic acid–acetate buffer solution is $[A^-]/[HA] = 1:0.573$. Each value is the average of two runs.

The variation of the rate with the nature of X substituent is moderate. Nevertheless, standard deviation values show that the differences among rate constants for compounds I–V are significant. Furthermore, we point out that (1) in water solutions the reactivity sequence is $k_{III} > k_{IV} > k_{II} > k_V > k_I$ (see Table II, pH 4.32); (2) on going from water to methanol all the rate constants increase; (3) in pure methanol the reactivity order becomes $k_I > k_{III} > k_{II} > k_V > k_{IV}$ ($k \times 10^4$ sec^{-1}: I, 193; III, 113; II, 86; V, 74; IV, 34).

In order to explain these results it seemed reasonable to propose a transition state in which the acid H atom bridges between N and S atoms.

Assuming that the π system is the same for every molecule here studied, the most significant σ-charges



are those located on nitrogen (1) and carbon (2) atoms of the bond that will break in the event of decomposition. The charge on the C-2 atom has a positive sign both in DTC$^-$ or DTCH and in the transition state model. Vice versa, the σ charge on the N-1 atom is negative in DTC$^-$ and DTCH species and positive in the transition state.[17] Consequently the N-1–C-2 linkage is greatly weakened and the CS_2 molecule can leave. This fact points up the importance of the inductive effect which, obviously, may be transmitted both through the ring and through the solvent.[18]

If only inductive effects are considered, the behavior of compound I in water solutions seems surprising. In fact, the CH_2 substituent is the weakest electron withdrawing and, therefore, compound I should be the most reactive. On the contrary, it is not only the last of the series, but it also shows the maximum activation energy value. Thus, it is necessary to examine experimental results in water–methanol mixtures.

The relation between ln k and the dielectric constant inverse, $1/D$, is typical of opposite sign reactant ions. Within the approximation of the use of eq 4,[19] which

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{kTDr^{\neq}} \qquad (4)$$

fits well for two simple ion reactions, the activated complexes radii can be estimated. The $r^{\neq}$ values so obtained are reported in the last line of Table V.

Although steric hindrance is of the same order of magnitude for all the molecules considered here (for the S atom only a ring distortion may be considered), compound I exhibits an $r^{\neq}$ value less than a half lower than the remaining compounds.

As far as the $\Delta S^{\neq}$ values are concerned, we observe that I shows a probability factor of *ca.* 10^{-4}, that is, 10–100 times higher than II–V. These facts could be tentatively interpreted as due to the lack (for X = CH_2) of the X-substituent contribution to the degree of charge dispersion in the activated complex.

In fact, on passing from pure water to pure methanol the reactivity series changes and becomes almost coherent with the predicted order for an inductive effect $-$I. Particularly, the rate constant values increase about ten times for I, which becomes the most reactive, and about three times for the remaining compounds. This points out the importance of the role of solvation in the reaction mechanism. For all compounds a stronger solvation makes the transfer process of the proton from sulfur to the nitrogen atom more difficult. For compound I, in which the X substituent is the least solvated, the decrease of the D value produces a faster rate-constant increase.

As far as the influence of ionic strength is concerned, the shape of the curve log k *vs.* $\mu^{1/2}$ is not linear (Figure 1). Nevertheless, in the wide μ range (0–1.00) ordinate value variation is moderate, being about 0.13 for compounds I–IV and 0.23 for compound V. The presence of a maximum clearly indicates that more than one factor is acting simultaneously and this probably arises from the complexity of the mechanism (see eq 3). Disagreement with expected behavior for opposite sign ions reaction is more marked at lower ionic strength values. This phenomenon could be tentatively attributed to a different interaction between the solvent and the solute molecules having many different charged sites.

To point up the role of the leaving group, the study of the diselenocarbamate decomposition mechanism is now in progress.

Experimental Section

Preparation and Characterization of Compounds.—All compounds were prepared by adding 1.1 mol of CS_2 to an ethyl ether solution of 1 mol of amine vigorously stirred with a 30% aqueous solution of 1 mol of NaOH and cooled by an ice bath (in the case of piperazine derivative only 1 mol of CS_2 was used). The compounds were twice recrystallized from ethyl ether–aqueous acetone and dried *in vacuo* over $CaSO_4$.

They were tested alcalimetrically, obtaining (I) $C_6H_{10}NS_2Na \cdot 2H_2O$, mol wt found 223.2, calcd 219.3; (II) $C_5H_8NOS_2Na \cdot 3H_2O$, mol wt found 241.2, calcd 239.3; (III) $C_5H_8NS_3Na \cdot 3H_2O$, mol wt found 254.0, calcd 252.3; (IV) $C_5H_9N_2S_2Na \cdot 2H_2O$, mol wt found 217.1, calcd 220.3; (V) $C_6H_{11}N_2S_2Na \cdot 3H_2O$, mol wt found 250.8, calcd 252.3.

Spectrophotometric Measurements.—The uv-visible spectra were recorded in freshly prepared aqueous solutions being 0.1 N in NaOH, using a Perkin-Elmer Model 402 or a Beckman DK 2A spectrophotometer. The ir spectra were recorded in the range 250–4000 cm^{-1} as KBr discs with Perkin-Elmer Model 325 equipment.

pH Measurements.—pH values were detected by a DAT 2002 pH meter equipped with a Lauda K2RD thermostat and a glass electrode (reference Ag/AgCl). Accuracy was ±0.01 pH unit.

Kinetic Measurements.—These measurements were carried out with a Perkin-Elmer Model 402 spectrophotometer connected to a Lauda K2RD thermostat (±0.02°). The spectra were periodically recorded in the range 230–310 nm, reading the absorbance values at the maxima wavelength. Each run was carried out in *pseudo*-first order conditions, *i.e.*, at a constant pH value, by adding, all at once, the proper amount of solid compound to a prethermostated buffer solution, obtaining a solution of about 10^{-4} M. Under these conditions the reaction product's absorbances were seen to be negligible. The detailed conditions of each run set are reported in the table explications.

Processing the Data.—Kinetic experimental data were processed by an H. P. 9100 B calculator. Straight lines were calculated by the least squares method and curves were well averaged by our special program of multiple regression, by obtaining the parameters of the equation $y = a + bx + cx^2 + dx^3$. Quantochemical calculations were carried out by means of a 1130 IBM computer.

Registry No.—I, 18474-20-9; II, 36976-42-8; III, 36976-43-9; IV, 36976-44-0; V, 36976-45-1.

Acknowledgments.—We wish to thank Miss Amelia Giuliani for her experimental contribution and the National Research Council (C. N. R.) for financial support.

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[17] This fact has been confirmed by means of a simple quantum-chemical calculation carried out by using the Del Re method. See G. Del Re, *J. Chem. Soc.*, 4031 (1958); F. Momicchioli and G. Del Re, *J. Chem. Soc. B*, 674 (1969).

[18] Recently the influence of an unconjugated sterically remote substituent on the rate process has been indicated as a "polar effect," including inductive and field effects. See L. M. Stock, *Chem. Educ.*, **49**, 400 (1972).

[19] O. H. Bamford and C. H. F. Tipper, "The Theory of Kinetics," Vol. II, Elsevier, Amsterdam, 1969, p 321.