N-Nitroamides and N-Nitrocarbamates. IV. Rates of Decomposition. A Case of Steric Acceleration[1]

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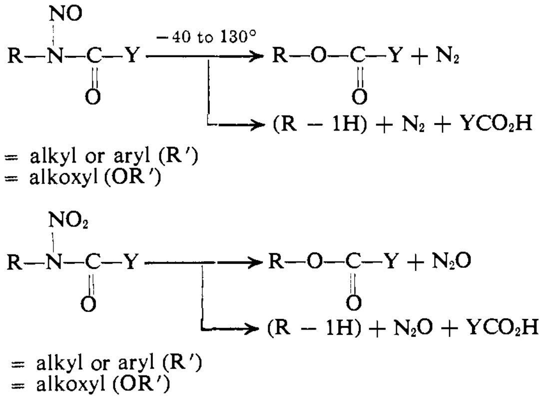
Abstract: The kinetics of thermal decomposition have been measured and activation parameters have been calculated for a series of N-alkyl-N-nitrocarbamates (IIb); the reactions are first order. Steric acceleration of the decomposition was found and the effect was shown to arise principally from a decrease in the heat of activation. Comparisons with the decompositions of N-nitrosocarbamates, N-nitroamides, and N-nitrosoamides were also made and it was found that the N-nitrocarbamates of bulky amines are abnormally stable relative to the corresponding N-nitrosocarbamates. That is, the N-nitrocarbamates, while showing a steric acceleration as a function of the size of the alkyl substituent, show it to a lower degree than the N-nitrosocarbamates. The effect is believed to arise from nonbonded interactions of the nitro group with the alkyl group R (in IIb) in the transition state.

A series of amide derivatives is known in which the members, all thermally labile, decompose to give similar sets of products. These derivatives are easily made by the nitrosation and nitration of the corresponding amides and carbamates. The kinetics of decomposition of the various types are similar in form and a comparison was deemed to be of interest.



$$R\text{—}\overset{NO}{N}\text{—}\underset{O}{\overset{\|}{C}}\text{—}Y \xrightarrow{-40\ \text{to}\ 130°} R\text{—}O\text{—}\underset{O}{\overset{\|}{C}}\text{—}Y + N_2 \quad \longrightarrow (R - 1H) + N_2 + YCO_2H$$

Ia, Y = alkyl or aryl (R′)
b, Y = alkoxyl (OR′)

(1)

$$R\text{—}\overset{NO_2}{N}\text{—}\underset{O}{\overset{\|}{C}}\text{—}Y \longrightarrow R\text{—}O\text{—}\underset{O}{\overset{\|}{C}}\text{—}Y + N_2O \quad \longrightarrow (R - 1H) + N_2O + YCO_2H$$

IIa, Y = alkyl or aryl (R′)
b, Y = alkoxyl (OR′)

Experimental Section

The N-nitrosocarbamates, the N-nitroamides, and the N-nitrocarbamates were prepared as reported previously.[2,3] The decompositions were followed in the ultraviolet at 330 mμ for compounds IIb (R = *t*-butyl and R = triethylcarbinyl) and at the band in the 230–240-mμ region for the others. Solutions were degassed in an all-glass apparatus to which was attached a quartz ultraviolet cell, and the apparatus plus cell was then sealed off under vacuum at 1–5 torr. An oil bath with a Sargent thermonitor as the regulator was used as the constant temperature bath; with this apparatus it was possible to maintain a given temperature to within 0.01°. The absolute temperature could be read to 0.1° and estimated to within 0.01° on a thermometer calibrated with a platinum resistance thermometer. However, due to large stem effects at temperatures above 120°, satisfactory reproducibility at these temperatures was attainable only by measuring the temperature directly with the resistance thermometer.

For each run, the cell was equilibrated at 22° and the initial absorbance (A_0) was determined on a Cary ultraviolet spectrometer, Model 14; air alone was used in the reference compartment. The sample was then placed in the heated bath, 60 sec being allowed for the sample to reach (with shaking) the bath temperature. At intervals, the cell was removed and placed in a hexane bath at 22°, 60 sec being allowed for the sample to reach 22° (with shaking). After 10 min at 22°, the cell was cleaned and the absorbance was determined. The temperature of the bath was monitored more frequently than the sample withdrawals to ensure constancy.

Runs varied from 1 to 6 half-lives, and five to ten points were used to establish the linearity of the first-order plots. An infinity reading (A_∞) was determined after *ca.* 10 half-lives (except in the case of the *n*-butyl derivative where the solvent absorbance was used as A_∞; this assumption seems justified in that in the other cases the final absorbance was very close to that of the solvent alone).

Rate constants and standard deviations from the mean as given in Table I were calculated through use of the "long interval" method.[4a] In all cases the data gave good first-order rate plots (log $(A - A_\infty)$ *vs.* t) and the rate constants determined from these by graphical methods were in good agreement with those obtained by the long interval method. In some cases the rate constants were also calculated by the method of least squares (Table I).

The activation parameters were calculated from the slopes of the best lines obtained on plotting log k *vs.* $1/T$ at three to seven different temperatures.[4b] The uncertainties reported represent the differences between the best line and a line drawn through the extreme points.

The commercial spectroscopic grades of acetonitrile and heptane were used without further treatment. They were found to be thermally stable at the maximum temperatures at which they were used in the degassed sample tubes. The decane used was treated as follows. Eastman practical grade decane (500 g) was stirred three times with 225-g portions of 15% fuming sulfuric acid for 6 hr. The hydrocarbon layer was washed with water between each acid wash. This treatment was followed by stirring the decane with two 150-g portions of fuming nitric acid. The decane was then stirred with calcium chloride and then with 14 mesh alumina. It was passed over a column composed of 120 g of 60–120 mesh silica gel and 120 g of basic alumina (the silica gel layer was above the alumina layer). The eluate was then distilled (30–42° at 5 torr). The product had an absorbance of 0.13–0.20 at 230 mμ in a 1-cm cell with air as the reference. The absorbance did not change when this decane (degassed and sealed off in an all glass apparatus) was heated at 150° for 3 days.

For the product study, 0.05–0.10 *M* solutions of methyl N-nitro-N-*sec*-butylcarbamate were heated at 140° for 3 days; decane was used as the solvent in the analysis of the esters, and hexadecane was used in the analysis of the olefins. The esters were analyzed by glpc on a 4-ft diisodecyl phthalate column at 130°. The olefins were analyzed by glpc on the same column attached in series to a 4-ft ethylene glycol–silver nitrate column at 25°. After the heating period, the tube containing the hexadecane solution was cooled in liquid nitrogen, opened, and quickly sealed to two gas traps in

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[1] Presented, in part, at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6, 1964, Abstracts, p 2N.

[2] (a) E. H. White, *J. Am. Chem. Soc.*, 77, 6008 (1955); (b) E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, 83, 1179 (1961); (c) E. H. White and D. W. Grisley, Jr., *ibid.*, 83, 1191 (1961); (d) E. H. White and R. J. Baumgarten, *J. Org. Chem.*, 29, 3636 (1964).

[3] Paper III: E. H. White, M. C. Chen, and L. A. Dolak, *J. Org. Chem.*, in press.

[4] "Technique of Organic Chemistry," Vol. VIII, A. Weissberger, Ed., 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1961: (a) R. Livingston, pp 126–134; (b) J. F. Bunnett, pp 199–202.

Table I. Rate Constants for the Decomposition of the Nitrocarbamates, $RN(NO_2)CO_2CH_3$ (IIb), and One Nitroamide, $RN(NO_2)COC_2H_5$ (IIa)

R	Solvent	Temp, °C	"Long interval" k, sec$^{-1\,a}$	Graphic value of k	Least squares k
n-Butyl (IIb)	Decane	120.15	$2.81 \pm 0.03 \times 10^{-6}$	2.78	
		120.15	2.97 ± 0.06	2.70	
		124.96	4.93 ± 0.07	5.02	
		125.00	5.17 ± 0.09	5.32	5.27
		129.31	8.60 ± 0.22	8.43	
		129.49	7.66 ± 0.07	7.68	
		135.41	15.3 ± 0.5	15.4	
sec-Butyl (IIb)	Decane	100.5	$5.50 \pm 0.19 \times 10^{-6}$	5.67	
		110.5	$1.62 \pm 0.06 \times 10^{-5}$	1.64	
		109.74	1.49 ± 0.11		
		130.4	$1.12 \pm 0.06 \times 10^{-4}$	1.16	
t-Butyl (IIb)	Decane	81.89	$3.24 \pm 0.10 \times 10^{-5}$	3.28	3.47
		85.60	4.87 ± 0.08	4.77	
		91.30	8.76 ± 0.14	8.67	
		98.0	$1.84 \pm 0.04 \times 10^{-4}$	1.86	2.07
		98.0	$1.99 \pm 0.05 \times 10^{-4}$	1.99	
		100.4	2.23 ± 0.13	2.28	
		100.4	2.46 ± 0.08	2.44	
	Acetonitrile	70.50	$2.38 \pm 0.26 \times 10^{-5}$	2.55	2.58
		75.55	4.03 ± 0.12	4.08	
		80.61	7.07 ± 0.22	7.28	
$(CH_3CH_2)_3C$ (IIb)	Heptane	25.0^b		6.98×10^{-7}	
		60.0^b		6.63×10^{-5}	
		80.0^b		6.13×10^{-4}	
Ethyl (IIa)	Heptane	71.21	$3.67 \pm 0.23 \times 10^{-5}$	3.78	
		80.70	$1.09 \pm 0.04 \times 10^{-4}$	1.08	
		90.65	2.89 ± 0.08	2.95	2.72

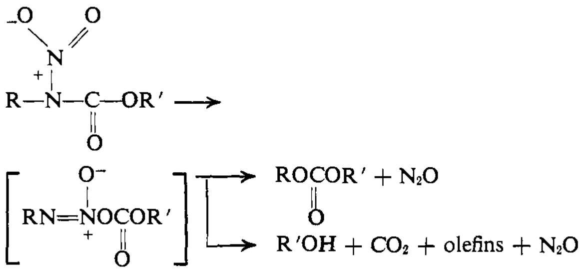
[a] Standard deviations are listed. [b] A resistance thermometer was not used in these runs; error probably ±0.06°.

series attached to the vacuum line. Dry Ice was used to cool the first trap and liquid nitrogen was used to cool the second. The system was evacuated and the hexadecane was raised to its boiling point. The second trap was then sealed off from the system and a limb was broken open under water. The volume was measured and the gases were analyzed by glpc (see text for data).

N-Nitrocarbamates (IIb). The nitrocarbamates are of particular interest, since of the four classes of related derivatives (I and II), the tertiary carbinamine member (I and II, R = *t*-alkyl) is stable and isolable only in series IIb (in all four cases, the rates of decomposition are determined largely by the size of the alkyl groups; *vide infra*). Furthermore, the nitrocarbamates are also abnormal in that they possess two carbonyl bands in the infrared spectra. The splitting was shown to result from rotational isomerism.[3] In studying this effect, evidence was also obtained for serious steric effects in the ground state of the more hindered nitrocarbamates. An attempt is made in the present study to relate the kinetics of decomposition to these factors.

The products of decomposition in this series[2c] are analogous to those obtained from the nitrosoamides.[2,5] As a further example, the products were determined for the decomposition of methyl N-nitro-N-*sec*-butylcarbamate in hydrocarbon solvents. Found were methyl *sec*-butylcarbonate (50%), 1-butene (24%), *trans*-2-butene (14%), *cis*-2-butene (9%), and methylcyclopropane (2%);[6] not present in the reaction mixture were methyl N-*sec*-butylcarbamate, isobutane, and butane.

Good first-order rate plots were obtained for the N-nitrocarbamates (Figure 1, Table I), and the Arrhenius plots (Figure 2) were also satisfactory. Checks at different concentrations by the half-period and differential methods confirmed the first-order nature of the decompositions. Difficulty was experienced with runs on the *t*-butyl derivative in decane in that a series of bands, the most prominent of which were at 324–335 mμ, appeared in the ultraviolet spectrum after about 2 half-lives. Using rigidly purified decane as the solvent, however, the decomposition could be followed almost to completion before the interfering bands appeared. Rates measured with the better batches of decane agreed well with the initial rates in the poorer batches. Also, the decomposition of

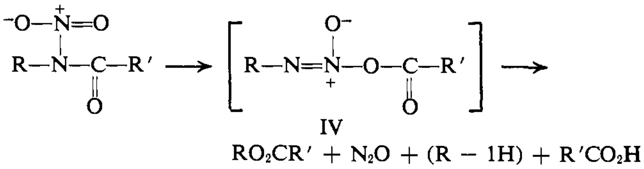


$$R{-}N(NO_2){-}C({=}O){-}OR' \longrightarrow \left[RN{=}\overset{O^-}{\underset{+}{N}}OC({=}O)R'\right] \begin{cases} \longrightarrow ROC(O)R' + N_2O \\ \longrightarrow R'OH + CO_2 + \text{olefins} + N_2O \end{cases} \qquad (2)$$

the *n*-butyl derivative was in no instance followed for more than 2 half-lives, since after this period the first-order plots showed a trend toward decreasing values of k. Blank runs with nitrous oxide in decane, and with nitrous oxide–1-butene mixtures in decane, showed that no products absorbing in the ultraviolet were formed from these compounds.

The rates of decomposition are not very sensitive to the nature of the solvent, a fact also true for the decomposition of the corresponding N-nitrosoamides (Ia).[7]

N-Nitroamides (IIa). The rates of amide nitration decrease sharply with an increase in size of the alkyl group R (I and II),[2a,c] and as a result, only nitroamides of primary and secondary carbinamines have been reported to date. The products of decomposition have been determined.[2c] Proof of the existence of the



$$R{-}N(\overset{+}{N}(O^-){=}O){-}C({=}O){-}R' \longrightarrow \left[R{-}N{=}\underset{+}{\overset{O^-}{N}}{-}O{-}C({=}O){-}R'\right] \longrightarrow$$

IV

$$RO_2CR' + N_2O + (R - 1H) + R'CO_2H$$

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(5) (a) E. H. White, *J. Am. Chem. Soc.*, **77**, 6011 (1955); (b) R. Huisgen and H. Reimlinger, *Ann.*, **599**, 183 (1956); (c) K. Heyns and W. V. Bebenburg, *Chem. Ber.*, **86**, 278 (1953).

(6) Cyclopropanes have been reported in related reactions by, *e.g.*, M. S. Silver, *J. Am. Chem. Soc.*, **82**, 2971 (1960); P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962); and G. J. Karabatsos, C. E. Orzech, and S. Meyerson, *ibid.*, **87**, 4394 (1965). Judging from the data of J. P. Chesick, *ibid.*, **82**, 3277 (1960), methylcyclopropane is stable at the reaction temperature we used (140°).

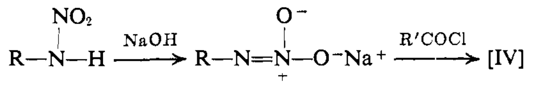
(7) K. Heyns and W. V. Bebenburg, *Ann.*, **595**, 55 (1955).

Table II. Rate Constants for the Decomposition of Various Nitrosoamides, Nitroamides, and Nitrocarbamates

Compound	Solvent	Temp, °C	k, sec^{-1}	Rate ratio
n-Butyl-N(NO)COCH$_3$	Xylene	90	7.59×10^{-3a}	*Ca.* 26
Ethyl-N(NO$_2$)COC$_2$H$_5$	Decane	90	2.70×10^{-4b}	
n-Butyl-N(NO)CO$_2$CH$_3$	Dodecane	90	4×10^{-6}	*Ca.* 54
n-Butyl-N(NO$_2$)CO$_2$CH$_3$	Decane	90	7.41×10^{-8c}	
Isopropyl-N(NO)COCH$_3$	Xylene	60	4.2×10^{-3d}	
sec-Butyl-N(NO)CO$_2$CH$_3$	Dodecane	90	2×10^{-4}	*Ca.* 10^2
sec-Butyl-N(NO$_2$)CO$_2$CH$_3$	Decane	90	1.86×10^{-6e}	
t-Butyl-N(NO)CO$_2$CH$_3$	CH$_2$Cl$_2$	0	*Ca.* 10^{-2}	*Ca.* 10^8
t-Butyl-N(NO$_2$)CO$_2$CH$_3$	Decane	0	4.4×10^{-10f}	
		90	7.52×10^{-5g}	
(C$_2$H$_5$)$_3$C–N(NO$_2$)CO$_2$CH$_3$	Heptane	90	1.65×10^{-3h}	

[a] See ref 7; extrapolated from value at 80°. [b] n-Butyl-N(NO$_2$)COCH$_3$ would have approximately the same rate, judging from the data in ref 9. [c] Extrapolated from 120°. [d] See ref 7. [e] Extrapolated from 100°. [f] Extrapolated from 81°. [g] Extrapolated from 91.3°. [h] Extrapolated from 80°.

mixed anhydride IV was obtained in this series through an independent synthesis.[2c,b] The stability of these compounds appears



$$\mathrm{R{-}\overset{\overset{\displaystyle NO_2}{|}}{N}{-}H \xrightarrow{NaOH} R{-}N{=}\underset{+}{\overset{\overset{\displaystyle O^-}{|}}{N}}{-}O^-Na^+ \xrightarrow{R'COCl} [IV]}$$

to be slightly greater than that of the corresponding N-nitrosoamides; kinetic data for the decomposition of the N-nitropropionamide of ethylamine are given in Table I.

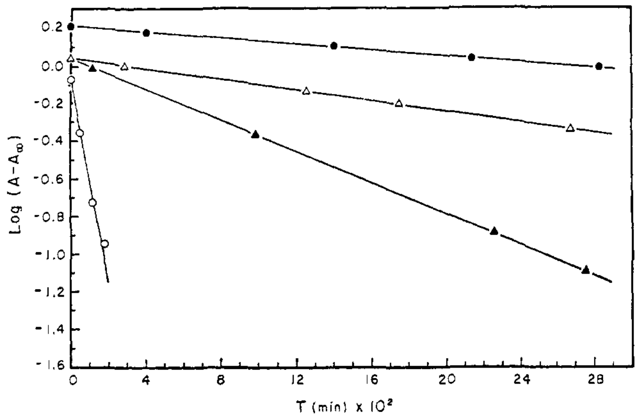


Figure 1. Rate plots for the decomposition of the N-nitrocarbamates (IIb) in decane: ●, R = n-butyl (at 130°); △, R = *sec*-butyl (at 100°); ▲, R = *sec*-butyl (at 110°); ○, R = t-butyl (at 100°).

N-Nitrosocarbamates (Ib). The products of the decomposition (eq 1) have been determined.[2a,d] Our rate constants were measured for a single run and they are less reliable than those determined for the other compounds.

The decomposition rates show a steep rise with the size of R (in Ib), and in fact, the nitrosocarbamates of tertiary carbinamines are not isolable at room temperature. An estimate of the rate of decomposition was made from the fact that the half-life of methyl N-nitroso-N-t-butylcarbamate (prepared at −25° from dinitrogen tetroxide and the carbamate in methylene chloride) in the reaction mixture was estimated to be *ca.* 100 sec at 0° (Table II). Since the decomposition rates for the nitrocarbamates and nitrosoamides appear not to be sensitive to the solvent, we assume that the rate constant here would not be much different in decane, the solvent used for the other nitrosocarbamates.

N-Nitrosoamides (Ia). The chemistry of the decomposition of these compounds (eq 1) has been amply documented.[2,6,8]

Discussion

The rate-determining step in all of these decompositions is the first[2c,9–11] (*e.g.*, as in eq 2). A comparison of the slow steps, as reflected in the rate constants (Table II), leads to four principal conclusions: (1) the carbamate derivatives are more stable than the amide derivatives; (2) the rates of decomposition increase with an increase in the size of the R groups, where, for the purposes of this paper, an increase in size means branching at the α-carbon atom; (3) the nitro derivatives are more stable than the corresponding nitroso compounds; and (4) the N-nitrocarbamates with tertiary R groups (IIb, R = t-butyl or triethylcarbinyl) appear to be abnormally stable relative to the N-nitrosocarbamate of t-butylamine.

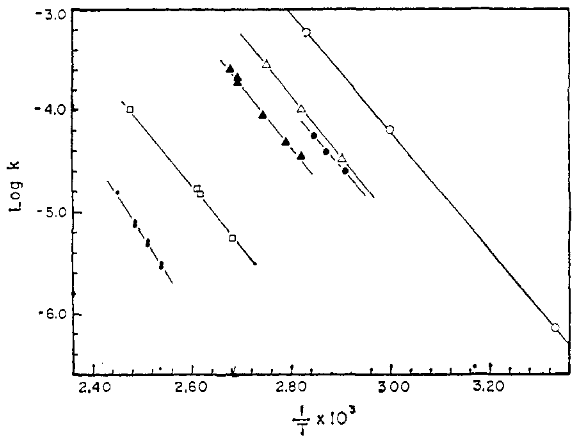


Figure 2. Arrhenius plots for the N-nitrocarbamates (IIb) and an N-nitroamide (solvent is decane, except where noted): ○, IIb, R′ = methyl, R = triethylcarbinyl; ▲, IIb, R′ = methyl, R = t-butyl; ●, IIb, R′ = methyl, R = t-butyl (in acetonitrile); □, IIb, R′ = methyl, R = *sec*-butyl; ●, IIb, R′ = methyl, R = n-butyl; △, N-ethyl-N-nitropropionamide.

The factor of about 10^3 in the stability difference between the amides and the carbamates (Table II) is in the right direction for an expression of the participation of the alkoxyl groups in resonance stabilization of the carbamates. Since the transition states for the decompositions do not involve resonance interactions

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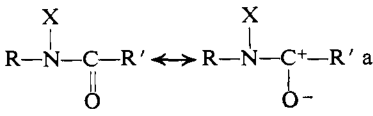
(8) In view of the great instability of the nitrosoamides and carbamates of tertiary carbinamines, it seems highly unlikely that the oil isolated by Heyns and Bebenburg[7] from the nitrosation of t-butylacetamide is N-nitroso-N-t-butylacetamide as claimed; the oil most likely represented products from the nitrosation of decomposition products of the nitrosamide.

(9) R. Huisgen and H. Reimlinger, *Ann.*, **599**, 161 (1956).

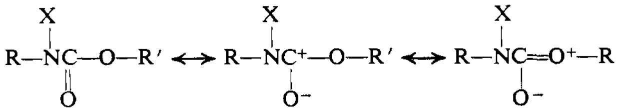
(10) R. Huisgen and C. Rüchardt, *ibid.*, **601**, 21 (1956).

(11) E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).



$$\mathrm{R{-}\overset{X}{N}{-}\underset{O}{\overset{\|}{C}}{-}R'} \longleftrightarrow \mathrm{R{-}\overset{X}{N}{-}\underset{O^{-}}{C^{+}}{-}R'}$$

as compared to

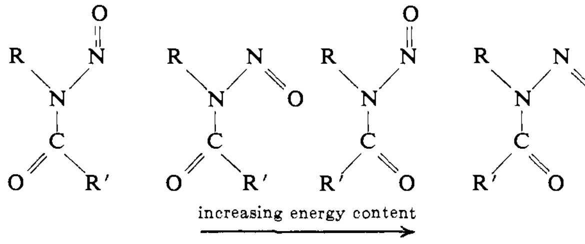


$$\mathrm{R{-}\overset{X}{N}\underset{O}{\overset{\|}{C}}{-}O{-}R'} \longleftrightarrow \mathrm{R{-}\overset{X}{N}\underset{O^{-}}{C^{+}}{-}O{-}R'} \longleftrightarrow \mathrm{R{-}\overset{X}{N}\underset{O^{-}}{C}{=}O^{+}{-}R}$$

of the alkoxyl group, or at least involve them to a lesser degree, a relative lowering of the ground state energy results and this, in turn, leads to an increase in the energy of activation. A similar rate difference (*ca.* 10^3 to 10^4) has been found for the rate of hydrolysis of acetyl chloride[12,13] (CH_3COCl) relative to that of methyl chloroformate[13] (CH_3OCOCl) in 10.9% aqueous acetone.

The effect of R on the decomposition rates of the nitrocarbamates is illustrated by the data of Table II; for the *n*-butyl, *sec*-butyl, and *t*-butyl nitrocarbamates, the rates at 90° increase in the ratio 1:25:1010. A discussion of the influence of the R groups is simplified by the observation that in related reactions electronic effects appear to be of little importance in determining the rates of decomposition. Huisgen and Reimlinger[9] have shown that the N-nitrosobenzamide and N-nitroso-*p*-nitrobenzamide of benzylamine differ in their rates of decomposition by only 2.2%; in addition, nitrosobenzamides of cyclohexylamine and aniline differ by only a factor of 2.6 in their rates (this factor includes the steric effect as well). The rate factors we have measured are well beyond the normal rate differences to be expected from the inductive effect, and we assume, in light of Huisgen and Reimlinger's work, that the major effect of R in compounds Ib, IIa, and IIb is steric in origin. Of course, as outlined above in the comparison of the amide and carbamate decompositions, if sufficiently dissimilar compounds are compared, electronic effects must be considered.

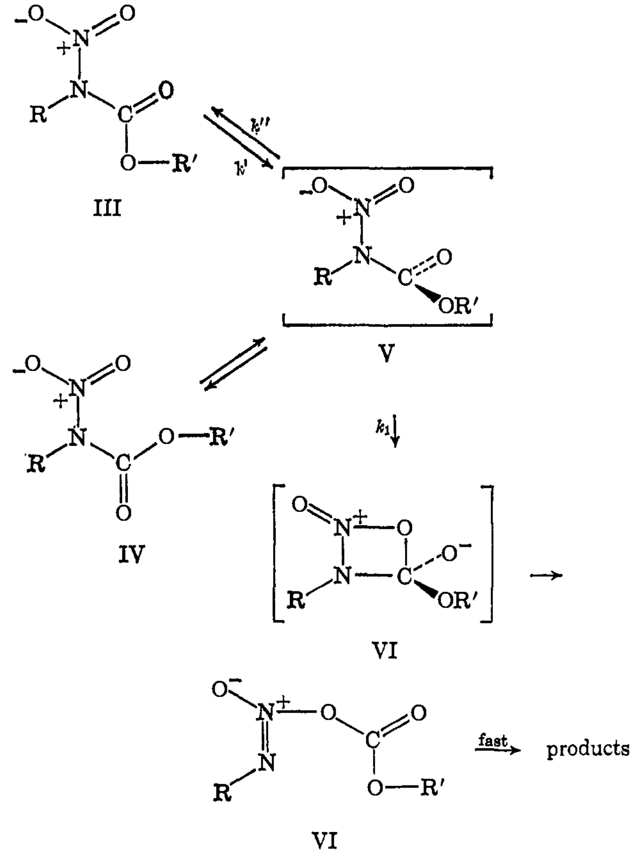
Huisgen and Reimlinger[9] have discussed the steric effects in the nitrosoamide decomposition in terms of the four isomeric planar forms of these compounds.



The energy content for the conformers listed increases from left to right as a result, largely, of increasing dipole–dipole interactions. Large R groups increase the population of the second form at the expense of the first form and thus they increase the energy of the ground state; a net decrease of the activation energy results (forms three and four are presumably negligibly populated).

In the nitrocarbamates, only two coplanar forms (III and IV) are possible, and our evidence shows that they differ but little in energy.[3] The physical data indicate, furthermore, that the rate of rotation (k', k'') of the carboalkoxy group is large relative to the decomposition rate;[3] k_1 is therefore the rate-determining step for the over-all decomposition (where VI represents the transition state; Scheme I). The

Scheme I



III

IV

V

VI

VI

interaction of the unshared p electrons of oxygen on the nitro group with the carbonyl group (in a direction perpendicular to the plane of the carbomethoxy group) follows from the usual view of nucleophilic attack on a carbonyl group.

The rate acceleration by large R groups is most easily understood in terms of nonbonded interactions of the R group with the nitro and carbomethoxy groups. The carbomethoxy interaction (and a part of the general nitro interaction) must be largely relieved in the transition state because of the near-perpendicular arrangement of the carbomethoxy group with respect to the molecular plane (Scheme I). To a first approximation, the transition state energies are independent of the size of R, whereas the ground state energies increase in proportion to the size of R; as a result, large R groups lead to a lowering of the activation energies and to a "steric acceleration."

From the activation parameters listed in Table III, it can be seen that the rate effect shows up largely in the activation energy term; this is consistent with the physical picture of the substituent effect as outlined above. The entropies of activation are small and insensitive to the size of the alkyl groups. Dominance of the activation energies has also been found in the decomposition of the N-nitrosoamides, and a few illustrative values are given in Table III.

Steric accelerations of a similar type have been reported for the Smiles rearrangement[14] and for the

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[12] E. J. Cairns and J. M. Prausnitz, *J. Chem. Phys.*, 32, 169 (1960).

[13] I. Ugi and F. Beck, *Chem. Ber.*, 94, 1839 (1961).

[14] J. F. Bunnett and T. Okamoto, *J. Am. Chem. Soc.*, 78, 5363 (1956).

Table III. Activation Parameters for the Decomposition of the Nitrocarbamates and Related Compounds

Compound	Solvent	E_{act}, kcal	ΔH^*, kcal	ΔS^*, eu
n-Butyl-N(NO$_2$)CO$_2$CH$_3$	Decane	34.3 ± 0.5	33.5 ± 0.5	-2.4
sec-Butyl-N(NO$_2$)CO$_2$CH$_3$	Decane	30.8 ± 0.2	30.0 ± 0.2	-4.6
t-Butyl-N(NO$_2$)CO$_2$CH$_3$	Decane	28.8 ± 1.2	28.1 ± 1.2	-2.2
	Acetonitrile	26.2 ± 0.2	25.5 ± 0.2	-3.7
$(C_2H_5)_3CN(NO_2)CO_2CH_3$	Heptane	25.9	25.2	-2
$C_2H_5N(NO_2)COC_2H_5$	Heptane	27.8 ± 1.5	27.1 ± 1.5	-2.5
n-Butyl-N(NO)COCH$_3$	Xylene	29.0[a]		
$C_6H_5CH_2$-N(NO)COCH$_3$	Psuedocumene	28.2[b]		
$C_6H_5CH_2$-N(NO)COC(CH$_3$)$_3$	Psuedocumene	21.4[b]		
Cyclohexyl-N(NO)COCH$_3$	Psuedocumene	23.3[b]		

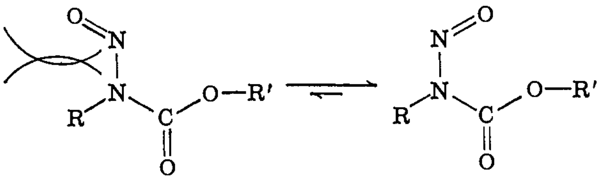
[a] Reference 7. [b] Reference 9.

rates of lactonization of substituted hydroxymethylbenzoic acids;[15] in both cases, the activation energy term accounted for the largest part of the rate increases. A case of steric acceleration in the solvolysis of esters of tertiary alcohols has also been reported.[16] The rate differences were relatively small, however, as were the differences in the activation parameters.

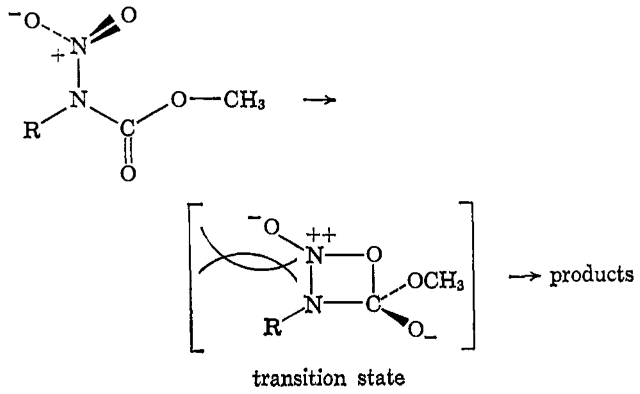
The third point, that the nitro derivatives are more stable, in general, than the nitroso analogs (Table II), could be explained by a greater nucleophilicity of the oxygen atom of the nitroso group relative to that of the oxygens of the nitro group. There seem to be no data in the literature bearing on this matter although the known propensity of the nitrosoalkanes to undergo tautomerization may be pertinent. Another possible explanation involves the nonbonded interaction of the second oxygen atom of the nitro group with the R group in the transition state of the decomposition; anticipating the discussion in the next section, this effect would raise the transition state energies for all of the nitro derivatives relative to those for the nitroso analogs. It is unlikely that a greater charge separation in the transition state for the nitrocarbamate decomposition is the answer since the rates appear not to change appreciably with solvent polarity (Table I).

The fourth point listed above deals with the stability of the nitrocarbamates of tertiary carbinamines (and presumably of nitrocarbamates with other large R groups) relative to the stability of the corresponding nitrosocarbamates (Table II and the section on nitrosocarbamates). Compound IIb (R = t-butyl, R′ = methyl) decomposes at an appreciable rate only at about 100°, whereas the IIa analog decomposes rapidly at 0°. It should be pointed out that nitrosoamides derived from tertiary carbinamines are also too unstable to isolate. For example, the nitrosoamide of the tertiary carbinamine (2-phenyl-2-butylamine) decomposes rapidly at −30°.[17] The relative stabilities of the n-, sec-, and t-butyl derivatives of the nitroso- and nitrocarbamates are given in Table II; the ratio 54: 10^2:10^8 (for rate NO/rate NO$_2$) increases sharply at the tertiary alkyl level. There is a sizeable error in our estimate of the rate of decomposition of methyl N-(t-butyl)-N-nitrosocarbamate, but the increase in the rate ratio far exceeds any possible error. This abnormally high stability of the nitrocarbamate member can be accounted for in terms of the differences in the sizes and shapes of the nitroso and nitro groups.

As discussed above, nonbonded interactions between the R and carbomethoxy groups that are relieved in the transition state lead to a steric acceleration of the decomposition. A second type of nonbonded interaction of the R groups involves the nitroso and nitro groups. In the nitroso derivatives, this interaction would raise the ground state energy (*via* an increase in the population of the *syn* form), but there



would be little effect on the transition state energy. In the nitro derivatives, because of the symmetry of the nitro group, this simple possibility of strain relief through rotation does not exist, and the interaction increases both the ground and transition state energies. Furthermore, the physical data suggest that in the ground state of highly hindered derivatives (R = t-alkyl), the nitro group is tilted somewhat out of the molecular plane.[3] In the transition state, the nitro



transition state

group (as part of a four-membered ring) would need to be in, or almost in, the molecular plane. As a consequence, nonbonded interactions of the nitro and R groups may well be greater in the transition state than in the ground state. The resulting increase in the activation energy (or at least its constancy if the ground and transition state interactions are the same) would thus account for the interesting relative stability

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(15) J. Tirouflet, *Bull. Soc. Chim. France*, 769 (1964); J. F. Bunnett and C. F. Hauser, *J. Am. Chem. Soc.*, **87**, 2214 (1965).

(16) P. D. Bartlett and M. Stiles, *ibid.*, 77, 2806 (1955).

(17) E. H. White and J. E. Stuber, *ibid.*, **85**, 2186 (1963).

of the nitro derivatives. In summary, the rate acceleration by large R groups is less for the nitro than for the nitroso compounds because of the extra and special interaction of the R group and the nearest oxygen atom of the NO_2 group in the transition state; in the case of substitution by *t*-alkyl groups, this factor appears to be very important indeed. It would be interesting to see whether a similar effect occurs in the decomposition of N-nitroamides of tertiary carbinamines.

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Classical General Base Catalysis of Silicon–Oxygen Bond Cleavage[1]

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Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas. *Received March 7, 1966*

Abstract: Phenoxytriphenylsilane (I) reacts with appropriately buffered solutions of methanol to form phenol and methoxytriphenylsilane according to the kinetic law given in eq 1, where k_1, k_2, and k_3 exhibit a Brønsted correlation with $\beta = 0.7 \pm 0.2$. The results are consistent with classical (proton transfer) general base catalysis but not with nucleophilic catalysis.

It has been shown by Åkerman[2] that aryloxysilanes undergo both acid- and base-catalyzed solvolyses in aqueous ethanol but react only very slowly, if at all, in neutral solutions. The base-catalyzed solvolysis could proceed, in buffered solution, according to any of four mechanisms formulated below. Several variations on each of these mechanisms may be generated by considerations of the rate-determining step and the possible intermediacy of higher coordination number derivatives of silicon.[3] Mechanism I can be distinguished from the other mechanisms since it is the only one which would show specific base catalysis. Mechanisms II, III, and IV are analogous to the nucleophilic catalysis (II), classical general base catalysis (III), and inverse classical general base catalysis (IV) mechanisms well known in the solvolysis of carboxylate derivatives.[4] We wish to report data which permit the closer specification of the mechanism for cleavage of the silicon-oxygen bond under these conditions.

Mechanism I

$$B + ROH \rightleftharpoons BH^+ + RO^- \quad \text{(rapid)}$$

$$RO^- + R_3SiOAr \longrightarrow R_3SiOR + ArO^-$$

$$BH^+ + ArO^- \longrightarrow B + ArOH \quad \text{(rapid)}$$

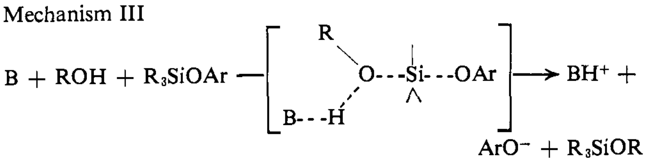
Mechanism II

$$B + R_3SiOAr \longrightarrow R_3SiB^+ + ArO^-$$

$$R_3SiB^+ + HOR \longrightarrow BH^+ + R_3SiOR$$

$$BH^+ + ArO^- \longrightarrow B + ArOH \text{ (rapid)}$$

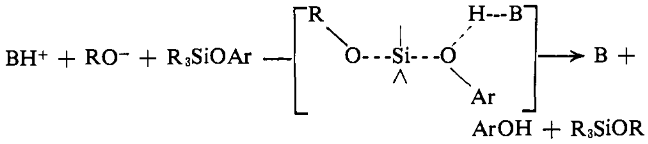
Mechanism III



$$ArO^- + BH^+ \longrightarrow B + ArOH \quad \text{(rapid)}$$

Mechanism IV

$$B + ROH \rightleftharpoons BH^+ + RO^- \quad \text{(rapid)}$$



Results

Table I shows observed and calculated rate constants for the methanolysis of phenoxytriphenylsilane (I) in

Table I.[a] Base-Catalyzed Methanolysis of Phenoxytriphenylsilane at 27.4 ± 0.1°

Buffer system	[B], M	[BH], M	[CH_3O^-], M	10^5k_{obsd}, sec^{-1}	10^5k_{calcd}, sec^{-1}
Acetate-acetic acid	0.0500	0.0100	2.50×10^{-7}	1.81	1.87
	0.1000	0.0200	2.50×10^{-7}	2.06	2.15
	0.1500	0.0300	2.50×10^{-7}	2.39	2.43
	0.0500	0.0050	5.01×10^{-7}	3.37	3.23
	0.1000	0.0100	5.01×10^{-7}	3.60	3.51
	0.1500	0.0150	5.01×10^{-7}	3.92	3.89
	0.0500	0.0033	7.51×10^{-7}	4.83	4.85
	0.1000	0.0067	7.51×10^{-7}	5.30	5.13
	0.1500	0.0100	7.51×10^{-7}	5.78	5.41
Phenoxide-phenol	0.0005	0.0100	1.15×10^{-4}	1020	1010
	0.0010	0.0200	1.15×10^{-4}	1200	1195
	0.0020	0.0400	1.15×10^{-4}	1580	1570

[a] Ionic strength brought to 0.1500 M with $LiClO_4$ in all runs. Uncertainties in observed rate constants are about ±5%.

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[2] E. Åkerman, *Acta Chem. Scand.*, **10**, 298 (1956); **11**, 373 (1957).

[3] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[4] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).