The Homolytic and Heterolytic Decomposition of N-Nitroso-N-acyl-O-alkylhydroxylamines[1,2]

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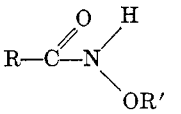
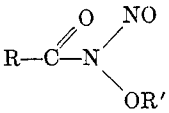
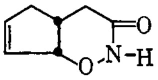
The nitrosation of N-acyl-O-alkylhydroxylamines (I) leads to N-nitroso derivatives (II) which have spectra similar to N-nitrosoamides (VI) and N-nitrosodialkylamines. The spontaneous decomposition of N-nitroso-N-acyl-O-alkylhydroxylamines occurs with the formation of nitrogen, carbon dioxide, nitrous oxide, and products resulting from either a homolytic or a heterolytic cleavage of the molecule. The two processes frequently occur simultaneously, and the amount of reaction by each path varies with the structure and reaction medium.

This study is concerned with the nitrosation of N-acyl-O-alkylhydroxylamines (I) and the reactions of the N-nitroso-N-acyl-O-alkylhydroxylamine products (II). Only one nitrosation of this type of compound, the cyclic N-acyl-O-alkylhydroxylamine III has been reported to produce an N-nitroso derivative IV which spontaneously decomposed to the lactone V in ethanol.[4] A heterolytic mechanism was proposed for the decomposition of IV.


I


II

a, R = Me; R′ = Et
b, R = Me; R′ = *n*-Pr
c, R = Me; R′ = *p*-nitrobenzyl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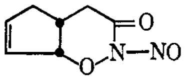
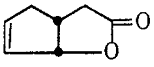
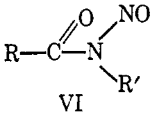
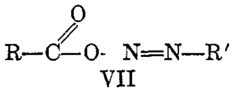

IV

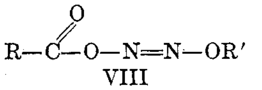

V


VI

The N-nitrosoamides VI are similar in structure to the compounds considered here, and several groups of workers led by Huisgen,[5] White,[6] and Hey[7] have made relatively recent studies of these compounds that have bearing on this research. Huisgen and co-workers have provided evidence that the N-nitroso-N-acylanilides (VI, R′ = Ar) slowly rearrange to diazonium esters VII which rapidly react to give the expected products. White's work has been concerned with the N-alkyl-nitrosoamides (VI, R′ = alkyl) and all his work has been interpreted as involving a slow rearrangement to aliphatic diazo esters which then decompose to esters or acids and olefins.

In this work it has been assumed that II slowly rearranges to the O-acyl-O′-alkyl hyponitrite (VIII) which then decomposes rapidly. Since the proposed intermediate is a hyponitrite, the several studies of related hyponitrites are relevant to this study. Symmetrical dialkyl hyponitrites have been prepared from silver hyponitrite and alkyl iodides[8–10] and were found to decompose to aldehydes and alcohols and to serve as free-radical initiators in polymerization reactions.[11] These reactions have been interpreted as involving the homolytic cleavage to nitrogen and two alkoxy radicals.[12] The mechanism of the polar decomposition of hyponitrous acid has been reported recently, but in this work a competing radical reaction had to be suppressed.[13] O-Alkylhydroxylamines suffer deamination with nitrous acid, and the mechanism was reported to involve an O-alkyl hyponitrite which decomposed by a heterolytic path in acid medium.[14] In our study it has been assumed that II rearranges to the hyponitrite VIII and that products could arise from homolytic or heterolytic fragmentation of VIII.


$\mathrm{R{-}C({=}O){-}O^{-}\;N{=}N{-}R'}$
VII


$\mathrm{R{-}C({=}O){-}O{-}N{=}N{-}OR'}$
VIII

Results and Discussion

The first attempts to synthesize the nitroso compounds II met with little success, and the earliest evidence for the existence of these came from the visible spectra (Figure 1) of solutions of freshly nitrosated N-acyl-O-alkylhydroxylamines. The three peaks in the visible spectra were observed to decrease more or less rapidly, and rate measurements showed half-lives between several minutes and over 100 min. at 30° in carbon tetrachloride. Table I lists the calculated first-order rate constants for a variety of the nitroso compounds. Among the more stable compounds of this series was N-nitroso-N-acetyl-O-*p*-nitrobenzylhydroxylamine (IIc), and eventually this compound was isolated as a crystalline solid which, when it was purified and in the crystalline state, was stable at room temperature for a period of 1 week. A sample was sent for

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(1) Taken in part from the M.S. Theses of P. T. J., June 1963, and W. D. G., June 1964, University of Idaho. We are indebted to the National Science Foundation for Grant G13289 in support of this work.

(2) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

(3) Supported by National Science Foundation Grant GE2593 for undergraduate research.

(4) W. E. Noland, J. H. Cooley, and P. A. McVeigh, *J. Am. Chem. Soc.*, **81**, 1209 (1959).

(5) (a) R. Huisgen and G. Horld, *Ann.*, **562**, 137 (1948); (b) R. Huisgen, *ibid.*, **573**, 163 (1951); (c) R. Huisgen and H. Wakaten, *ibid.*, **573**, 181 (1951); (d) R. Huisgen and H. Reimlinger, *ibid.*, **599**, 161 (1956); (e) R. Huisgen and C. Ruchardt, *ibid.*, **601**, 21 (1956).

(6) (a) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955); (b) E. H. White, *ibid.*, **77**, 6011 (1955); (c) *ibid.*, **77**, 6014 (1955); (d) E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1174 (1961); (e) *ibid.*, **83**, 1179 (1961); (f) E. H. White and J. E. Stuber, *ibid.*, **85**, 2168 (1963).

(7) D. H. Hey, J. Stuart-Webb, and G. H. Williams, *J. Chem. Soc.*, 4657 (1952), and earlier papers in this series.

(8) W. Zorn, *Ber.*, **11**, 1630 (1878).

(9) A. Hantzsch and L. Kaufmann, *Ann.*, **292**, 329 (1892).

(10) J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2582 (1932).

(11) I. Harris, I. Marshall, and K. R. Jarrett, *Nature*, **159**, 843 (1947).

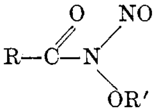
(12) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(13) J. R. Buchholz and R. E. Powell, *J. Am. Chem. Soc.*, **85**, 509 (1963).

(14) J. E. Leffler and A. A. Bothner-By, *ibid.*, **73**, 5473 (1951).

TABLE I

FIRST-ORDER RATES OF DECOMPOSITION OF II



$R-C(=O)-N(NO)-OR'$

R	R′	Medium	Temp., °C.	Method of measurement	$k \times 10^5$, sec.$^{-1}$
CH_3	C_2H_5	CCl_4	30	425 mμ	10.0 ± 0.5
				1750 cm.$^{-1}$	10.0
			40	425 mμ	34.5 ± 0.5
		CCl_4 with I_2	30	Nitroso 425 mμ	8.1
				I_2 510 mμ	7.4
				Nitroso 425 mμ	8.4
				I_2 510 mμ	8.1
		CCl_4 with I_2 and $CHCl_2COOH$		Nitroso 425 mμ	20
				I_2 510 mμ	18
		CCl_4, HCOOH, and I_2		Nitroso 425 mμ	Fast
CH_3	*p*-Nitrobenzyl	CCl_4	30	425 mμ	7.6
					6.0[a]
		CH_3COOH	30	425 mμ	9.4
CH_3	*n*-Propyl	CCl_4	30	425 mμ	10.5
CH_3	Benzyl	CCl_4	30	425 mμ	11.5
C_2H_5	*n*-C_3H_7	CCl_4	30	425 mμ	32
i-C_3H_7	*n*-C_3H_7	CCl_4	30	425 mμ	130
C_6H_5	Benzyl	CCl_4	30	425 mμ	240
m-Nitrophenyl	*n*-C_3H_7	CCl_4	30	425 mμ	76.0
p-Tolyl	Benzyl	CCl_4	30	425 mμ	Fast
CH_3	C_2H_5	1 *M* in CCl_4	30	1750 cm.$^{-1}$	Not first order
CH_3	C_2H_5	CCl_4	30	Volume of gas	Not first order

[a] This nitroso compound was isolated and purified in this run.

microanalysis, and the results were in agreement with the expected. IIa and IIb were found to be yellow liquids at room temperature and could be volatilized at low pressures and room temperature, but these compounds decomposed rapidly and exothermically when kept at room temperature.

The absorption spectra for II agree with the expected. Figure 1 shows a comparison of the visible spectra of IIa, λ_{max} 425, 407, and 390 mμ, with that of N-nitroso-N-butylacetamide, λ_{max} 432, 416, and 400 mμ. The latter compound was prepared by White,[6b] and reprepared for spectrographic analysis in this laboratory. Recently the spectra of N-nitrosodialkylamines have been published, and they resemble those in Figure 1 with absorption maxima at 378, 365, and 355 mμ.[15] Extinction coefficients of about 130 were determined for II, while Noland[4] has reported 115, 129, and 93 for λ_{max} at 439, 418, and 402, respectively, of IV. The infrared spectrum of II showed C=O near 1730 cm.$^{-1}$ and N=O near 1520 cm.$^{-1}$, while White[6a] has reported C=O near 1730 cm.$^{-1}$ and N=O near 1515 cm.$^{-1}$ for VI and Noland[4] has reported 1748 cm.$^{-1}$ for the carbonyl of IV. The n.m.r. spectrum of IIc showed the expected two doublets in the aromatic region, a deshielded methylene singlet, and a methyl group singlet.

Among the first observations of the decomposition of II have been the rates of decomposition. These rates are easily obtained by observing changes in the visible spectra with time, but it is also possible to use infrared absorptions. Rate measurements by gas evolution have not been successful. Plots of log absorbance against time have given good straight lines in all cases

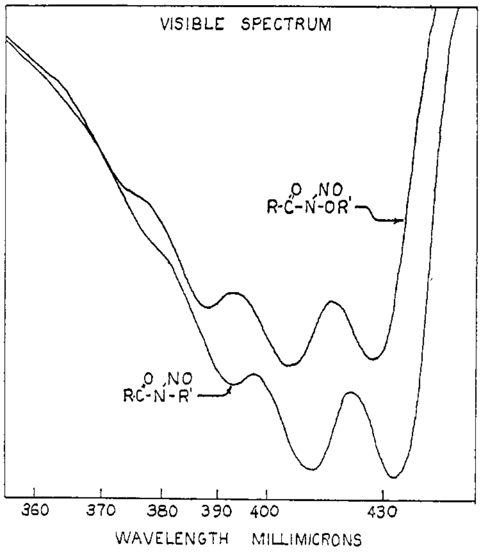


Figure 1.

studied provided that solutions of approximately 0.005 *M* concentration or less were used. Changes in solvent from carbon tetrachloride to acetic acid had a very minor effect on the rate. In general the rate studies parallel those of Hey and co-workers[7] and Huisgen and co-workers[5] and are consistent with a slow rearrangement of II to VIII.

A free-radical decomposition of VIII similar to what has been suggested for the dialkyl hyponitrites calls for the formation of nitrogen, free alkoxy radical, and free acyloxy radical. The latter would be expected to eliminate carbon dioxide and form the alkyl or aryl free radical more or less readily. Nitrogen and carbon dioxide are among the gases observed, and, when IIa de-

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(15) W. S. Layne, H. H. Jaffé, and H. Zimmer, *J. Am. Chem. Soc.* **85**, 435 (1963).

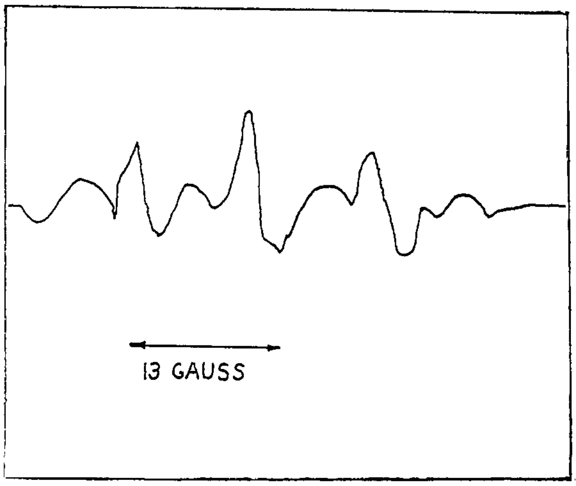

Figure 2.—E.p.r. spectrum of IIa in benzene using a Varian V-4502 e.p.r. spectrometer and a peroxylaminedisulfonate standard.

composed in cyclohexane, methane was also observed to be in an amount equal to the carbon dioxide formed. Also consistent with the formation of methyl free radical from II where R is methyl were the observations that methyl iodide resulted when the solvent was carbon tetrachloride and iodine was present, that methyl chloride was found when the solvent was carbon tetrachloride, and that nitromethane was formed when dinitrogen tetroxide was present. Our search for evidence in favor of alkoxy radicals was for a time unsuccessful. The decomposition of IIb in carbon tetrachloride with added iodine produced methyl iodide, and should have produced *n*-propoxy free radicals which were expected to eliminate formaldehyde and form ethyl radicals.[12,16,17] The latter were expected to form ethyl iodide. Neither formaldehyde nor ethyl iodide were found in this reaction, and formaldehyde has never been observed in any of these decompositions. Evidence in favor of alkoxy radicals was obtained from the decomposition of IIc in carbon tetrachloride containing dinitrogen tetroxide, an excellent scavenger for alkoxy radicals. The product, *p*-nitrobenzyl nitrate was formed in excellent yield.[18] The product analysis has provided evidence in favor of the expected homolytic cleavage for VIII.

Further evidence in favor of a homolytic cleavage in this reaction is found in the electron paramagnetic resonance (e.p.r.) spectra. Thus IIa in benzene showed a seven-line spectrum containing rather broad peaks shown in Figure 2. A similar spectrum was obtained by decomposing IIa on Molecular Sieve 5A.[19]

The heterolytic decomposition of VIII patterned after the known decomposition of hyponitrites requires the formation of nitrous oxide, which has usually been found in these decompositions. At this time it cannot be stated which of the oxygens of the hyponitrite go to form the nitrous oxide, and, furthermore, it is uncertain if rearrangement of II to VIII is necessary for the formation of nitrous oxide. In the decomposition of IIc in aqueous acetic acid with a trace of sulfuric acid the gas was purely nitrous oxide, and a nearly quantitative yield of *p*-nitrobenzyl alcohol was obtained. When the sulfuric acid was not included both carbon dioxide and nitrous oxide were observed and no alcohol was found. The acid catalysis may be explained as involving a protonation of either of the hyponitrite oxygens followed either by cleavage to the acylium ion, nitrous oxide, and alcohol or cleavage to carboxylic acid, nitrous oxide, and the carbonium ion. Useful comparisons may be made to the work of Leffler[14] and to studies by Crawford and Raap[20] on the acid-catalyzed decomposition of N,N′-dicarbalkoxy-N,N′-dialkoxyhydrazines. Both groups of workers have suggested that protonation on alkyl oxygen is the prelude to the heterolytic decomposition, and the latter workers have suggested that an acylium ion is produced in the related decomposition.

Of the variety of products that have been isolated from these decompositions many could originate from either a heterolytic or a homolytic decomposition. Alcohols could come from alkoxy radicals, and when IIc was allowed to decompose in cyclohexane carbon dioxide, methane, and *p*-nitrobenzyl alcohol were obtained. *p*-Nitrobenzyl alcohol was also observed in the heterolytic decomposition. Esters could originate in a heterolytic process or by acetolysis of alkyl nitrates. The latter compounds form in the free-radical reaction and are known to suffer heterolysis quite readily.[21] Benzyl nitrate has been found to form benzyl acetate under the conditions of many of our experiments. In most of the decompositions studied nitrous oxide, nitrogen, and carbon dioxide were found, and the ratio of homolytic to heterolytic reaction was assumed to be reflected by the ratio of carbon dioxide to nitrous oxide.

Tables II–IV show the ratio of nitrous oxide to carbon dioxide under varying circumstances. Table II deals with changes in ratio with solvent changes. Al-

TABLE II

RATIO OF NITROUS OXIDE TO CARBON DIOXIDE FROM THE N-NITROSO-N-ACETYL-O-ETHYLHYDROXYLAMINE DECOMPOSITION WITH DIFFERENT SOLVENTS[a,b]

CCl_4, ml.	Added solvent (ml.)	$N_2O:CO_2$
5	Formic acid (2)	∞
5	Ethanol (5)	∞
5	Dichloroacetic acid (5)	2.5
5	Pyridine (4)	1.5
5	Formamide (immiscible)	0.5
6	None	0.065[c]
2	Cyclohexane (6)	1.37
0	glacial acetic acid	2.0

[a] All temperatures were 30° unless otherwise specified. [b] The initial concentration was about 1 *M* and the analysis was carried out after the reaction was complete. The infrared spectrum of the gas which was evolved from a 0.1 *M* solution of N-nitroso-N-acetyl-O-ethylhydroxylamine in carbon tetrachloride showed only a peak at 2350 cm.$^{-1}$. The solution which remained showed only this same peak. Under similar circumstances both the 2350-cm.$^{-1}$ peak and the 2250- and 2210-cm.$^{-1}$ peaks were observed in the gas which was evolved from N-nitroso-N-acetyl-O-*p*-nitrobenzylhydroxylamine. [c] At 50°.

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(16) C. F. Wuster, Jr., L. J. Durham, and H. S. Mosher, *J. Am. Chem. Soc.*, **80**, 327 (1958).

(17) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 443.

(18) It has been suggested that a nitrate could form by the reaction of an alkoxide ion with dinitrogen tetroxide. This has not been found to be the case, and sodium benzyloxide with dinitrogen tetroxide gave benzyl nitrite, benzyl alcohol, benzaldehyde, and benzoic acid. No benzyl nitrate was detected.

(19) C. B. Colburn, R. Ettinger, and F. A. Johnson, *Inorg. Chem.*, **2**, 1305 (1963); **3**, 455 (1964).

(20) R. J. Crawford and R. Raap, *J. Org. Chem.*, **28**, 2419 (1963).

(21) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1192, 1208 (1955); J. W. Baker and A. J. Neale, *ibid.*, 609 (1955).

TABLE III

VARIATIONS OF THE GAS RATIO WITH STRUCTURAL CHANGES[a,b]

N-Acyl	O-Alkyl	$N_2O:CO_2$
Aceto	Ethyl	0.21
Isobutyro	*n*-Propyl	0.074
Benzo	Benzyl	0.01
m-Nitrobenzo	*n*-Propyl	0.04

[a] At 30°. [b] The initial concentration was 1 *M* and the reaction was complete when the gas analysis was made. The ratio of nitrous oxide to carbon dioxide evolved from N-nitroso-N-acyl-O-*n*-propylhydroxylamine as determined by infrared spectra was found to vary also with the series aceto > propiono > isobutyro.

TABLE IV

CHANGES IN THE CARBON DIOXIDE TO NITROUS OXIDE RATIO DURING THE DECOMPOSITION OF N-NITROSO-N-ACETYL-O-ETHYLHYDROXYLAMINE[a,b]

Run 1		Run 2[c]	
Time, min.	$CO_2:N_2O$	Time, min.	$CO_2:N_2O$
30	24.5	45	1.5
75	26.1	60	2.0
105	6.9	75	2.9
135	3.0	105	4.4
165	1.8	120	5.3
195	1.5	135	5.7
225	1.3	165	4.4
24 hr.	0.9	195	3.7
		285	2.1

[a] A 1.5 *M* solution of the hydroxylamine in carbon tetrachloride was used; temperature was 30°. [b] Approximately 10-cc. aliquots were removed during the decomposition from the total gas evolved and no correction was made for the gas removed. Total volume of gas was estimated at 650 cc. [c] Solution saturated with nitrous oxide.

though the more polar solvents favor the formation of nitrous oxide, there is not a clear correspondence here. Table III indicates the change in gas ratio with structural changes. If VIII is assumed to produce a carboxylic acid anion in the heterolytic decomposition, these data could be explained as reflecting the stability of such anions. Table IV shows the changes in gas ratio as the reaction progresses. At first carbon dioxide was the predominant product, but as the reaction progressed more and more nitrous oxide was formed. It seems quite likely that products of the reaction may be catalyzing the formation of nitrous oxide. The studies on the ratio of nitrous oxide to carbon dioxide indicate that the decomposition of II frequently involves two competing paths.

Experimental

N-nitroso-N-acetyl-O-*n*-propylhydroxylamine (IIb).—N-Acetyl-O-*n*-propylhydroxylamine was prepared according to the methods previously described.[22] The nitrosation procedure used was the method of White[6a] for the nitrosation of amides with dinitrogen tetroxide. To a solution of 1.158 g. (0.0099 mole) of N-acetyl-O-*n*-propylhydroxylamine in 10 ml. of carbon tetrachloride, which had been purified by passing through a column of alumina and distilling, was added 1.7 g. of freshly dried sodium acetate. This slurry was cooled to between −10 and −20° and 0.7 ml. (0.017 mole) of dinitrogen tetroxide measured at 0° was added through a capillary tube while the mixture was stirred and kept under slightly reduced pressure with an aspirator. When all of the dinitrogen tetroxide was added, the solution was filtered, washed with ice-cold 5% sodium bicarbonate, and dried with 3 pellets of potassium hydroxide. An infrared spectrum at this time revealed that the N–H and 1670-cm.$^{-1}$ C=O bands of the starting compound had disappeared. The solvent was removed using a rotary film evaporator and maintaining the temperature between −10 and −20°. The residual yellow oil, 1.295 g., 91%, was then transferred to a Hickman still where it volatilized at 2-mm. pressure and room temperature and 0.837 g. (58%) was collected in a receiver cooled with Dry Ice. A sample, 0.0552 g. in 100 ml. of carbon tetrachloride, showed absorbances of 0.410 at 425 mμ, 0.455 at 4.06 mμ, and 0.295 at 390 mμ which were used to calculate extinction coefficients of 115, 127, and 83 at the three respective wave lengths. These absorbances were corrected for the rate of decomposition and zero time was the instant that the solution was prepared. A first-order rate constant at 30.00 ± 0.01° was calculated as 10.5 × 10^{-5} sec.$^{-1}$ using this equation.

$$k = 2.303/t \log (A_0 - A_\infty)/(A_t - A_\infty)$$

The absorbance at infinite time was taken as the absorbance at a time when no further change was observed. The infrared spectrum of the pure liquid showed C=O at 1760 cm.$^{-1}$ and N=O at 1520 cm.$^{-1}$.

N-Nitroso-N-acetyl-O-*p*-nitrobenzylhydroxylamine (IIc).—A mixture of 2.10 g. (0.01 mole) of N-acetyl-O-*p*-nitrobenzylhydroxylamine and 2.1 g. of sodium acetate in 25 ml. of carbon tetrachloride at 0° was saturated with dinitrogen tetroxide and allowed to stand for 10 min. The mixture was filtered, washed with 5% sodium carbonate and then water, and dried with magnesium sulfate. After the solution had been cooled for 12 hr. in a deep freeze (−25°), 1.3 g. (54%) of pale yellow crystals had formed, m.p. 66–67° dec. This product was dissolved in carbon tetrachloride at room temperature and reprecipitated at −25° and, after several such recrystallizations, the melting point increased to 74° dec.

Anal. Calcd. for $C_9H_9N_3O_5$: C, 45.19; H, 3.79; N, 17.56. Found: C, 45.38; H, 4.33; N, 17.13, 16.83.[23]

An extinction coefficient (ϵ 137) and first-order rate of decomposition (k = 7.0 × 10^{-5} sec.$^{-1}$) at 30.00 ± 0.01° were determined using the absorption maxima at 425 mμ and a Perkin-Elmer 4000A Spectracord. The absorption maxima at 406 and 390 mμ were blocked by a stronger absorption of the *p*-nitrobenzyl group.

Other N-Nitroso-N-acyl-O-alkylhydroxylamines.—The same method of preparation was used as in the preparation of IIb. Characteristic absorption bands of the starting N-acyl-O-alkylhydroxylamines, 3400 (NH) and 1600 (CO) cm.$^{-1}$, disappeared upon combination of the reagents. In general, attempts to isolate the N-nitroso compounds failed. Evaporation of the solvents resulted in explosive decompositions. When purification by column chromatography was attempted, the yellow bands disappeared on the columns of sugar, alumina, or silica gel, before elution with a solvent could be completed. The visible spectra of all the preparations showed absorption maxima at 425, 406, and 390 mμ (Figure 1) and infrared bands at 1760–1730 (CO) and near 1530 (NO)cm.$^{-1}$.

Rate Measurements.—The first-order rates of disappearance of the N-nitroso-N-acyl-O-alkylhydroxylamines were measured spectrophotometrically using the absorption maxima at 425 mμ or at 1750 cm.$^{-1}$. In general the concentrations were not known, but a starting absorbence of about 0.6 (concentration of about 0.005 *M*) was used. A circulating, constant-temperature bath set at 30 ± 0.01° and a constant-temperature cell holder were used for the measurements at 425 mμ. When the 1750-cm.$^{-1}$ absorption was used, the solution was kept in the constant-temperature bath and aliquots were transferred to a 3-mm. cell. In several runs iodine was included in about 0.0008 *M* concentration and then was observed to disappear. In order to observe the changes in nitroso compound and iodine simultaneously it was necessary to work at the different concentrations because the ϵ for IIa was 113 while that for iodine was reported to be 900.[24] Using the ϵ value of 105 for the 425-mμ band of IIa, the relative rates of disappearance are 0.10 for iodine and 1.0 for the nitroso compound. A similar run with IIc indicated relative rates of 0.07 for iodine to 1 for the nitroso compound.

Gaseous Products.—The qualitative analysis of the gaseous products was carried out by gas chromatography using a Molecular Sieve 5A column and by infrared absorption bands at 2350 cm.$^{-1}$ for CO_2 and a doublet at 2250 and 2210 cm.$^{-1}$ for N_2O. Gases with the same retention time as methane, nitrogen, oxygen, nitrous oxide, and carbon dioxide were observed when a sample

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[22] J. H. Cooley, W. D. Bills, and J. R. Throckmorton, *J. Org. Chem.*, **25**, 1743 (1960).

[23] Analysis was performed by Elek Microanalytical Laboratories, Torrance, Calif.

[24] O. J. Walker, *Trans. Faraday Soc.*, **31**, 1435 (1935).

of N-nitroso-N-acetyl-O-ethylhydroxylamine was decomposed. Some of the nitrogen and some or possibly all of the oxygen arose from air which was not rigorously excluded.

Ratio of Gases.—A 1.0-g. (0.01-mole) sample of N-acetyl-O-ethylhydroxylamine was nitrosated in carbon tetrachloride as described before and allowed to decompose in a vacuum line. The high-boiling gases were condensed in a Dry Ice trap, and samples of the low-boiling gases were withdrawn using a gas syringe and analyzed using a Molecular Sieve 5A column at 30° and at 148°. At 30° peaks due to oxygen and nitrogen were observed. The oxygen was believed to have come from the atmosphere and a quantitative correction for atmospheric nitrogen was applied based on this assumption. At 148° peaks corresponding to methane, nitrous oxide, carbon dioxide, and a combination of nitrogen and oxygen were observed. The area ratio of methane–nitrous oxide–carbon dioxide–nitrogen was found to be 1:1.7:8.6:7.8. These areas were corrected for thermal conductivity and then were 1:1.3:6.1:6.9.

Quantitative Determination of Nitrogen-Containing Gases.—N-Nitroso-N-acetyl-O-ethylhydroxylamine was prepared from 0.8140 g. (0.007910 mole) of N-acetyl-O-ethylhydroxylamine and 0.61 g. (0.01 mole) of dinitrogen tetroxide as described before. The solution was not filtered or extracted with 5% sodium bicarbonate but was connected directly to a Dry Ice trap and a vacuum line. The pressure change and volume indicated the formation of 0.01661 mole of gas. Gas chromatographic analysis indicated the formation of 0.00418 mole of carbon dioxide, 0.00014 mole of methane, 0.00473 mole (60%) of nitrogen, and 0.00294 mole (37%) of nitrous oxide. The total nitrogen and nitrous oxide was 0.00767 mole or 97%.

Methyl Iodide from IIb.—A sample of N-acetyl-O-*n*-propylhydroxylamine (1.17 g., 0.01 mole) was nitrosated in carbon tetrachloride and decomposed at reflux temperature with 2.54 g. (0.02 mole) of iodine. The reaction mixture was distilled, and the distillate was weighed and analyzed by gas chromatography on a silicone oil column at 70°. The mixture contained peaks with the same retention times as methyl iodide and carbon tetrachloride, and the ratio of peak areas indicated that 0.31 g. (22%) of methyl iodide was formed. The infrared spectrum was identical with that of methyl iodide.

Decomposition of IIa in Cyclohexane.—A 0.01-mole sample of N-acetyl-O-ethylhydroxylamine was nitrosated in 10 ml. of carbon tetrachloride. This solution was extracted with cold sodium bicarbonate, concentrated to 2 ml., and combined with 6 ml. of cyclohexane. The mixture, which was connected to a vacuum line, was decomposed at 30° during a 2-day period. The ratio of gases was nitrous oxide–carbon dioxide–methane, 1.37:1:1. A black insoluble tar had settled out of solution by the time the reaction was complete. Gas chromatographic analysis using a polypropylene glycol column at 170° showed materials with retention times identical with ethyl acetate, acetic acid, ethanol, and acetaldehyde in a ratio of 1:0.31:0.05:0.03. Only the identity of the peak corresponding to ethyl acetate was confirmed by infrared analysis.

***p*-Nitrobenzyl Nitrate from IIc.**—A solution containing 0.10 g. (4.2×10^{-4} mole) of IIc in 10 ml. of dry carbon tetrachloride was saturated with dinitrogen tetroxide and left overnight at room temperature. When the solvent was removed under reduced pressure and the solid residue was recrystallized from petroleum ether (b.p. 30–60°), 0.07 g. (84%), m.p. 66–67°, was obtained. A melting point of 71° has been reported for *p*-nitrobenzyl nitrate.[25] A mixture melting point with material obtained from the reaction of *p*-nitrobenzyl bromide with silver nitrate was 67–68°. The infrared spectra of the two samples were identical.

IIc in 50% Acetic Acid Containing Sulfuric Acid.—A mixture of 0.196 g. (8.2×10^{-4} mole) of IIc with 5 ml. of acetic acid, 5 ml. of water, and 3 drops of concentrated sulfuric acid was warmed for a few minutes and allowed to stand. The gases from the mixture showed only nitrous oxide absorption peaks in the infrared. When the solution was evaporated and the residue was recrystallized from water, 0.122 g. (96%), m.p. 94–95.5°, m.p. (with *p*-nitrobenzyl alcohol) 94–95.5°, was obtained. The infrared spectrum was identical with that of *p*-nitrobenzyl alcohol.

IIc in Cyclohexane.—Cyclohexane was purified by washing with concentrated sulfuric acid, passing through a column of alumina, and distilling, and was saturated with iodine. To 25 ml. of cyclohexane was added 0.162 g. (6.8×10^{-4} mole) of IIc, the mixture was placed in a 250-ml. flask which was partially evacuated with an aspirator and sealed, and the flask and its contents were heated to 50°. After 12 hr. an infrared spectrum of the gases showed carbon dioxide absorption at 2350 cm.$^{-1}$ and no nitrous oxide absorption at 2250 and 2210 cm.$^{-1}$. When the solvent was removed, 0.113 g. of solid remained. Part of this solid (0.093 g., 6.07×10^{-4} mole, 91%) dissolved in hot petroleum ether and then precipitated upon cooling. This solid was identified as *p*-nitrobenzyl alcohol by its infrared spectrum. The residue, 0.020 g., was an unknown compound of m.p. 126–128° dec. with a C=O absorption at 1720 cm.$^{-1}$ in the infrared spectrum.

Nitrosation of N-Benzyl-O-benzylhydroxylamine.—A solution of 4.530 g. (0.0201 mole) of N-benzoyl-O-benzylhydroxylamine was nitrosated with 1.5 ml. (0.025 mole) of dinitrogen tetroxide in 300 ml. of carbon tetrachloride.[26] After 15 min. the solution was filtered, washed with 5% sodium bicarbonate, and dried with anhydrous magnesium sulfate. The solution was connected to a gas line and allowed to decompose for 20 hr. The infrared spectrum of the gases indicated carbon dioxide and methyl chloride to be present but no nitrous oxide was shown. The solvent was removed under reduced pressure and the residue was chromatographed on 450 g. of Alcoa activated alumina. The following products were obtained: benzyl benzoate, 0.607 g. (14.3%), contaminated with a trace of benzyl nitrate, and eluted with petroleum ether; benzyl acetate,[27] 1.03 g. (34%), eluted with benzene; benzyl alcohol, 0.252 g. (11.2%), eluted with chloroform; benzamide, 0.072 g., 2.4% eluted with ether. A tar and several unidentified components were also observed.

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[25] E. L. Homes and C. K. Ingold, *J. Chem. Soc.*, **127**, 1810 (1925).

[26] Solutions of dinitrogen tetroxide in carbon tetrachloride have been studied by R. E. Turley and are sometimes explosive: *Chem. Eng. News*, **42**, No. 47, 53 (1964).

[27] The acetate group must have originated with sodium acetate.