

expand F in eq. 2 in a Taylor series about the value obtained from the initially specified parameters, F^0

$$F' = F^0 + \sum_p \frac{\partial F^0}{\partial X_p} \Delta X_p + \frac{1}{2!} \sum_{p,q} \frac{\partial^2 F^0}{\partial X_p \partial X_q} \Delta X_p \Delta X_q + \dots \quad (4)$$

where the X_p values are the parameters K , A , and B which are to be optimized. If our initial assumptions of values for the latter are reasonable, we may truncate eq. 4 after the first-order sum term, which linearizes our statistical problem.

Therefore

$$F_i'(\text{comp.}) - F_i(\text{obsd.}) = \Delta F_i' = \Delta F_i^0 + \sum_p \frac{\partial F_i^0}{\partial X_p} \Delta X_p \quad (5)$$

and

$$\frac{1}{2} \frac{\partial \sum_i (\Delta F_i')^2}{\partial X_j} = \sum_i \Delta F_i^0 \frac{\partial F_i^0}{\partial X_j} + \sum_i \sum_p \frac{\partial F_i^0}{\partial X_p} \frac{\partial F_i^0}{\partial X_j} \Delta X_p = 0 \quad (6)$$

Here, $\partial F_i^0 / \partial A = (y^0 / [D_0])_i$, $\partial F_i^0 / \partial B = (([D_0] - y^0) / [D_0])_i$, and $\partial F_i^0 / \partial K = (\partial F_i^0 / \partial y)(\partial y / \partial K) = ((A - B) / [D_0])_i (y^0 / P'(y^0))_i$, where $P'(y) = \partial P(y) / \partial y$.

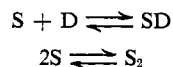
The problem is now one of solution of eq. 3 in terms of y and then of the simultaneous equations (6); the latter yield the values for X_p . Since $X_p' = X_p + \Delta X_p$, new values for A , B , and K are obtained. Using these, the procedure is repeated until either all parameters converge or the standard deviation for fitting converges within prespecified limits between consecutive cycles.

The procedures adopted have been illustrated for the special case of 1:1 SD complexing; however, several

other complexing situations of interest can also be considered upon minor changes in parts of the analysis. For example, for dimerization of the solute, $K_{\text{dissocn}} = [D]^2 / [D_2]$, the only change required in the above analysis is in eq. 3, *i.e.*

$$4y^2 - (4[D_0] + K)y + [D_0]^2 = P(y) = 0 \quad (7)$$

and in the partial derivatives, $\partial F_i / \partial K$, derived from it. Further, for cases where more than one process of importance occurs, *e.g.*



two equilibrium constants enter but eq. 1, 2, 5, and 6 still apply. With this understanding, the Fortran coded program constructed for use on the IBM 7094 (and later modified for the IBM 7074) was written as a main program with a set of subroutines one for each complexing case. The former, completely general for all cases of interest, accepts the initial parameter choices, sets up eq. 6, solves them, and tests the new parameter values. The subroutines generate only the appropriate partial derivative sums which are used in eq. 6.

The following statistical quantities are derived directly: the data variances, $V_i = \Delta F_i$, correct to the first-order sum term in ΔX ; the parameter variances, equivalent to σ^2 : goodness of fit (GoF) = $\sum_i V_i^2 / (ND - NP)$, where ND is the number of data and NP the number of parameters fitted (the standard deviation of fitting is obtained from this quantity); the inter-parameter correlation coefficients, ρ_{pq} . The absolute value of this quantity is between 0 and 1; the closer to one, the stronger is the linear dependence of X_p on X_q .

Carbalkoxynitrenes. The Photolytic Decomposition of Gaseous Alkyl Azidoformates¹

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The photolytic decomposition of gaseous ethyl and methyl azidoformates has been studied with regard to carbalkoxynitrene formation and other modes of decomposition. Chemical trapping and product analysis show that the nitrenes are produced when light is used whose energy is above about 95 kcal./mole, but below 130 kcal. Transient spectra show absorption by NCO. From the appearance time of NCO and the dependence of the NCO spectrum on partial pressure of a chemical trapping agent, limits on the nitrene lifetime are set at about 3×10^{-7} and 10^{-5} sec. At higher photolysis energies transient N_3 is also observed, and the product

pattern indicates that a transient but unobserved CO_2N_3 may be present.

Introduction

Transient polyatomic species supposedly containing monovalent nitrogen (nitrenes) have been identified in

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gas phase^{4,5} and in solution.^{6,7} The states and properties of these substances are still only understood at a primitive level, either in terms of electronic states or of gross reactivity. Following the demonstration⁷ that azidoformates (I) decompose photolytically *via* a nitrene intermediate (II), we have investigated these particular systems in the gas phase in an attempt to



elucidate the properties and structure of moderately stable nitrenes. We have attacked the problem of identifying the transient intermediates by trapping them chemically, by analyzing the products, and by taking flash absorption spectra of the system after photolysis (flash-kinetic spectroscopy).

The first results of this investigation showed that flash photolysis of I gave a variety of transient products which seem to follow from more than one mode of decomposition of the photoexcited species.⁵ The results did show that the nitrene II is probably present as a photolysis product. We report here on the subsequent study of photolyses of simple alkyl azidoformates and related species and present the conclusions that can be drawn and the new questions that have arisen from the results from the spectroscopic and analytical methods.

Experimental

A. Apparatus. Flash photolyses were carried out with the equipment described in the preliminary account of this work and previously.^{5,8} Both single-pass and multiple-pass optical cells were used, so that light paths between 0.3 and 3.2 m. could be obtained. The photolysis flash lamp was usually a helix of fused silica tubing 4 mm. in diameter surrounding the sample cell. Energies up to 3 kjoules were dissipated in the flash lamp; the first half-period of this dissipation as measured by a simple inductive loop lasted less than 10 μ sec. The spectral flash, a fused silica capillary, was triggered by a delay circuit whose initiating signal came from a photocell watching the photolysis lamp.

Some spectra were taken on a rotating drum-camera spectrograph, whose optical system was designed by Dr. Carl David. This spectrograph had a wave length coverage of only about 25 $m\mu$, so that it was only useful for studying the time dependence of bands of known location. Other spectra were taken with a Bausch and Lomb medium quartz spectrograph and with a McPherson 2.217-m. concave grating spectrograph.

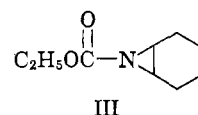
B. Photolyses. Materials for photolysis, the methyl and ethyl azidoformates and pivaloyl azide, $(\text{CH}_3)_3\text{C}-$

$(\text{CO})\text{N}_3$, were supplied by Dr. Thomas Mattingly and were used without further purification. Liquid samples were degassed and then allowed to vaporize to pressures near their equilibrium, room-temperature pressures, about 20 torr. Argon, nitrogen, and CO_2 each were used as moderating gases at pressures of about 0.5 atm. to keep the photolytic processes nearly isothermal. Carbon dioxide was the most effective stabilizer of the three.

Photolyses were carried out with the flash apparatus just described, and also with a photochemical reactor (Southern New England Ultraviolet Co.) in studies of products from continuous irradiation.

Yields, estimated from the amounts of stable products recovered, were only 1–2% when silica sample tubes were used, and lower when other tubes were substituted.

C. Chemical Trapping. Chemical trapping experiments were carried out with cyclohexene at a partial pressure of approximately 20 torr, and with an additional 0.5 atm. of carbon dioxide to ensure the removal of excess vibrational energy in the product. Both flash and steady photolyses were used. In the flash work, samples were subjected to several flashes of about 1.9 kjoules each. The contents were frozen in a cold finger at -190° and dissolved in pentane. Steady photolyses were carried out for 2 hr. and the products were collected in CCl_4 . The solutions were injected onto a vapor chromatograph column (20% Dow SF-96 on 40–60 firebrick at 150°). That material was collected whose retention time was that of 7-carboethoxy-7-azabicyclo[4.1.0]heptane (III). Three such collections provided enough material to obtain an infrared spectrum. The principal bands, 2980, 2940, 2860, 1720, 1430, 1350, 1270, 1210, 1080, and 1010 cm^{-1} , were those of III.



D. Product Identification. Stable products were determined primarily by v.p.c. retention times. Determinations of N_2 and H_2 were entirely unambiguous with a single 5A (Analabs) Molecular Sieve column. For other materials, with the exception of acetaldehyde, two or three different columns were used, as indicated in Table I. No successful method was found for identifying traces of formaldehyde in our mixtures.

Transients were determined, so far as possible, from their ultraviolet absorption band spectra. The NCO spectrum was studied in detail by Dixon⁴; the N_3 radical spectrum was obtained by Thrush.⁹ We have observed the bands listed in Table II. The intensity of the NCO absorption relative to that of N_3 was greater when CH_3OCON_3 was photolyzed than when $\text{C}_2\text{H}_5\text{OCON}_3$ was used.

Results and Conclusions

This discussion is most easily divided into two parts. First we examine the gross mechanism, draw some firm conclusions, and present one speculation which can be checked in a future experiment. Then we present a rather meager discussion of the electronic state of the nitrene intermediate.

(4) See, for example, the NCO radical: R. Holland, D. W. G. Style, R. N. Dixon, and D. A. Ramsay, *Nature*, **182**, 336 (1958); R. N. Dixon, *Phil. Trans. Roy. Soc. London*, **A252**, 165 (1960); *Can. J. Phys.*, **38**, 10 (1960).

(5) R. S. Berry, D. Cornell, and W. Lwowski, *J. Am. Chem. Soc.*, **85**, 1199 (1963).

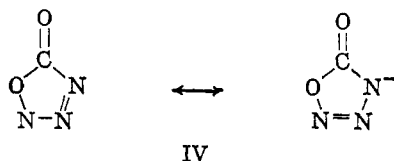
(6) W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962).

(7) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963).

(8) R. S. Berry, G. N. Spokes, and R. M. Stiles, *ibid.*, **84**, 3570 (1962).

(9) B. A. Thrush, *Proc. Roy. Soc. (London)*, **A235**, 143 (1956).

or if both bonds were simultaneously broken, we would find no simple mechanism to account for the formation of N_2O . If, on the other hand, the primary process leading to eq. 2b were cleavage of the alkyl-oxygen bond, then a mechanism is available. The transitory fragment CO_2N_3 might well be invoked as the progenitor of N_2O , proceeding through an intermediate IV which is capable of decomposing into N_2O and NCO .

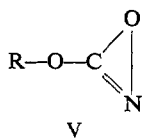


The lifetime of IV need only be long enough to permit the N-O bond to form, and we can present no evidence that such an intermediate is actually detectable. On the other hand the possibility is certainly open that CO_2N_3 has a long enough life to be observed, for example in a time-of-flight mass spectrometer.

Finally we turn to the question of the electronic state and structure of the carbalkoxynitrenes. Certainly $RO(CO)N$ is formed in a singlet state if the rule of spin conservation is obeyed. Otherwise, N_2 would necessarily appear in a triplet state. The half-life of the lowest triplet of N_2 is about 10^{-2} sec.¹¹ and would have been detectable in absorption if it were present in our systems. In fact careful searching revealed no sign of the strong and well-known first positive bands of N_2 or any other absorption system of triplet nitrogen. We conclude that it is very unlikely that the initial state of $RO(CO)N$ is triplet.

One other piece of negative evidence argues for the singlet assignment. When I ($R = C_2H_5$ or C_6H_5) was photolyzed in a glass at low temperature, Smolinsky, Wasserman, and Yager found no evidence in the microwave (e.s.r.) region for any stable triplet corresponding to II.¹²

At this point we must examine in a little more detail the electronic structure of the singlet carbalkoxynitrene. The electronic levels are sketched in Figure 1. According to structure II, the level π_2 is localized on nitrogen and n_1 is localized on oxygen, while π_1 is delocalized between C and O. An alternative structure is V, which differs from II only in degree—the degree to which π_2 is delocalized between C and N, n_1 is delocalized between O and N, and π_1 is localized on



oxygen. (Incidentally, if π_2 and n_2 were degenerate, the ground state would be a triplet.) The structure V would lead us to expect only a single strong $\pi_2 \rightarrow \pi_3$ excitation, probably at quite short wave lengths,

(11) A. N. Wright, R. L. Nelson, and C. A. Winkler, *Can. J. Chem.*, **40**, 1094 (1962).

(12) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

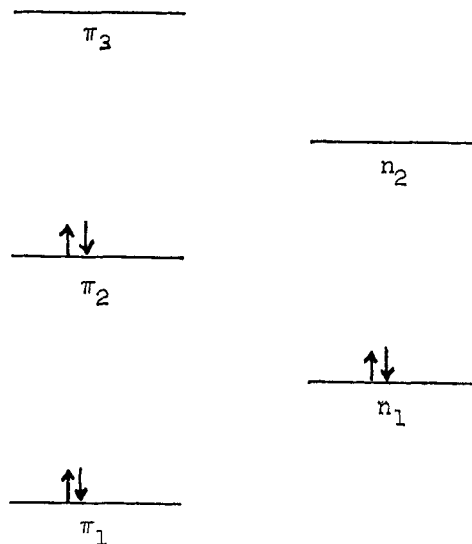


Figure 1. Orbital level scheme for the carbalkoxynitrenes. The orbitals are denoted as follows: π implies a linear combination of 2p orbitals of N, C, and (carbonyl) O whose axes are perpendicular to the NCO plane; n implies an orbital whose axis lies in the NCO plane; of these, π_1 is largely on O or between O and C, bonding them together; π_2 is rather localized on N or between N and C; π_3 (normally empty) is the most antibonding π -orbital and is localized primarily on carbon; n_1 is either localized on O or, if it overlaps enough with the in-plane p-orbital of N, becomes an O-N bonding orbital; and finally, n_2 is either localized on N or is antibonding with respect to N and O.

and a weak $\pi_2 \rightarrow n_2$ excitation. This is in somewhat better accord with our observations than the expectations from structure II.

The absorption spectra of transient species could only be investigated between about 900 and 250 $m\mu$ because the starting material is opaque between 250 and 200 $m\mu$ under our conditions. We did not observe any bands which could be attributed to the nitrene. Therefore we can only say that our evidence at hand is slightly more consistent with a singlet than with a triplet structure, and that of the possible singlets V again seems slightly more probable.

Obviously V is not a traditional nitrene structure at all. However since it differs from II only in degree and not in kind, we shall refer to both as nitrenes for convenience, at least until it is known which is the more accurate representation of the molecule.

We conclude by summarizing our more general conclusions. The photolytic decomposition of azidoformates I in the gas phase proceeds by two mechanisms. The low-energy mechanism produces a transient carbalkoxynitrene whose lifetime is between 3×10^{-7} and 10^{-5} sec.; the evidence is weakly in favor of assigning the nitrene as a singlet, perhaps as V. The higher energy mechanism probably proceeds through a transient CO_2N_3 intermediate whose lifetime is unknown.

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