

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  $P'(y) = \partial P(y) / \partial y$ .

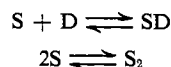
The problem is now one of solution of eq. 3 in terms of  $y$  and then of the simultaneous equations (6); the latter yield the values for  $X_p$ . Since  $X_p' = X_p + \Delta X_p$ , new values for  $A$ ,  $B$ , and  $K$  are obtained. Using these, the procedure is repeated until either all parameters 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  $\Delta X$ ; the parameter variances, equivalent to  $\sigma^2$ : 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,  $\rho_{pq}$ . 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 Azidoformates<sup>1</sup>

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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  $3 \times 10^{-7}$  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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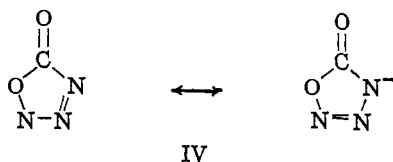
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or if both bonds were simultaneously broken, we would find no simple mechanism to account for the formation of  $N_2O$ . If, on the other hand, the primary process leading to eq. 2b were cleavage of the alkyl-oxygen bond, then a mechanism is available. 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  $NCO$ .

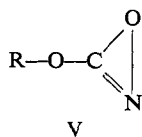


The lifetime of IV need only be long enough to permit the N-O bond to form, and we can present no evidence that such an intermediate is actually detectable. On the other hand the possibility is certainly open that  $CO_2N_3$  has a long enough life to be observed, for example in a time-of-flight mass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

Finally we turn to the question of the electronic state and structure of the carbalkoxy nitrenes. 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.<sup>11</sup> 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.<sup>12</sup>

At this point we must examine in a little more detail the electronic structure of the singlet carbalkoxy nitrene. The electronic levels are sketched in Figure 1. According to structure II, the level  $\pi_2$  is localized on nitrogen and  $n_1$  is localized on oxygen, while  $\pi_1$  is delocalized between C and O. An alternative structure is V, which differs from II only in degree—the degree to which  $\pi_2$  is delocalized between C and N,  $n_1$  is delocalized between O and N, and  $\pi_1$  is localized on



oxygen. (Incidentally, if  $\pi_2$  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).

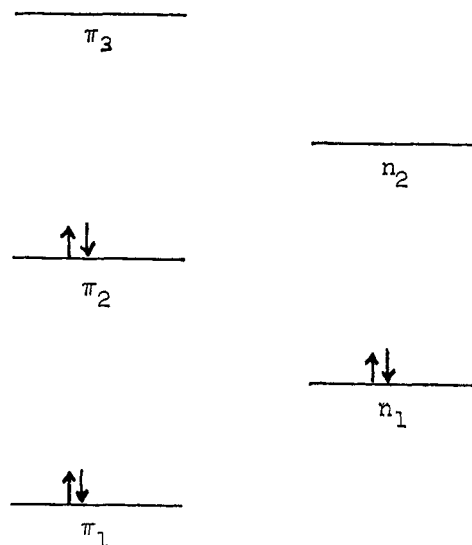


Figure 1. Orbital level scheme for the carbalkoxy nitrenes. The orbitals are denoted as follows:  $\pi$  implies a linear combination of 2p orbitals of N, C, and (carbonyl) O whose axes are perpendicular to the NCO plane;  $n$  implies an orbital whose axis lies in the NCO plane; of these,  $\pi_1$  is largely on O or between O and C, bonding them together;  $\pi_2$  is rather localized on N or between N and C;  $\pi_3$  (normally empty) is the most antibonding  $\pi$ -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 carbalkoxy nitrene whose lifetime is between  $3 \times 10^{-7}$  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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