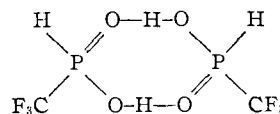


any interpretation implying much more monomer, the usually very strong  $3600\text{ cm.}^{-1}$  band surely would be expected to appear.

A distinct band of medium intensity at  $1071\text{ cm.}^{-1}$  is attributed to an O-H bending by analogy with the assignments which we have made for the  $(\text{CF}_3)_2\text{POH}$  molecule and further confirmed by means of the  $(\text{CF}_3)_2\text{POD}$  spectrum. An equally intense band at  $999\text{ cm.}^{-1}$  is not readily identifiable but may be due to complex motion within the cyclic dimer framework



The presence of bands corresponding to P-H and P=O stretching vibrations, as well as the O-H—O vibrations in the expected regions, are all strongly in favor of the phosphinic acid dimer structure and against the quadruply H-bridged  $\text{CF}_3\text{P}(\text{OH})_2$  dimer. Thus the spectrum confirms the indications from the energetics of the vapor-phase equilibria.

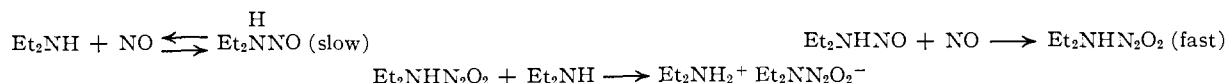
[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, CHEMISTRY DEPARTMENT, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

## A Mechanism for the Reaction of Diethylamine with Nitric Oxide

BY RUSSELL S. DRAGO, RONALD O. RAGSDALE<sup>1</sup> AND D. P. EYMAN

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Kinetic data are presented in support of a mechanism for the reaction of diethylamine with nitric oxide. The mechanism shown for formation of the product,  $\text{Et}_2\text{NH}_2^+\text{Et}_2\text{NN}_2\text{O}_2^-$ , is consistent with the observed kinetic data

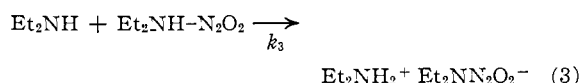
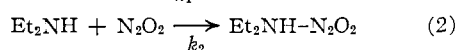
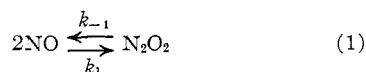


An activation energy of about 12 kcal. is obtained for the reaction.

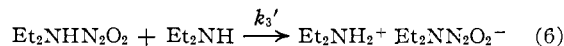
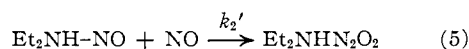
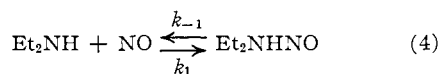
### Introduction

In an earlier article<sup>2</sup> it was shown that nitric oxide reacts with diethylamine to produce the compound  $\text{Et}_2\text{NH}_2^+\text{Et}_2\text{NN}_2\text{O}_2^-$ . Structural evidence was presented. By extending<sup>3</sup> this reaction to a whole series of amines it was demonstrated that this is a general reaction type for nitrogen(II) oxide.

Two possible mechanisms for this reaction were considered. One involves the attack of base on the nitric oxide dimer. Although detectable quantities of  $\text{N}_2\text{O}_2$  are not observed under reaction conditions, a kinetically important amount may exist resulting in the reaction path (I)



A second possible mechanism (II) is outlined



A kinetic study was undertaken to provide information concerning the reaction mechanism.

(1) Abstracted in part from the Ph.D. Thesis of R. O. Ragsdale, University of Illinois, Urbana, Ill. (1960).

(2) R. S. Drago and F. E. Paulik, *J. Am. Chem. Soc.*, **82**, 96 (1960).

(3) R. S. Drago and B. R. Karstetter, *ibid.*, **83**, 1819 (1961).

### Experimental

**Purification of Reagents. Diethylamine.**—Purification of diethylamine was necessary to prevent erratic results. Reagent grade diethylamine was refluxed 2 to 3 hr. over barium oxide. The middle fraction obtained upon distillation was stored in a desiccator and employed in these experiments.

**Nitric Oxide.**—Nitric oxide was purified by bubbling through 10 *M* KOH and dried by passing over solid NaOH pellets.

**Methanol.**—Reagent grade methanol was employed.

**Apparatus.**—A Cary Recording Spectrophotometer Model 14 was used for recording the ultraviolet spectra. Matched 1.00 cm. quartz cells with ground glass stoppers were employed. Polyethylene film was fastened over the stopper with a rubber band to prevent loss of nitric oxide to the atmosphere. No change was observed in the spectra of nitric oxide solutions over a period of 24 hr. The base line was checked every 30 minutes during a kinetic run.

**Extinction Coefficient Determinations.**—Nitric oxide was absorbed into a methanol solution from a gas buret. The experiment was conducted in a closed system and the volume of nitric oxide absorbed was measured. In three different experiments a value of  $\epsilon_{\text{NO}}$  equal to  $52 \pm 1$  (l. mole<sup>-1</sup> cm.<sup>-1</sup>) was obtained at  $346\text{ m}\mu$ . This frequency was selected to follow the appearance of product. It was also demonstrated that nitric oxide obeys Beer's law in the concentration range employed. The extinction coefficient of nitric oxide was found to increase upon the addition of amine. The value of  $\epsilon_{\text{NO}}$  in the presence of amine was determined by extrapolating back to zero time, readings obtained for the first 30 minutes after the addition of amine to an NO solution. A value of  $\epsilon_{\text{NO}} = 54 \pm 1$  l. mole<sup>-1</sup> cm.<sup>-1</sup> was obtained.

The product of the reaction  $\text{Et}_2\text{NH}_2^+ \text{Et}_2\text{NN}_2\text{O}_2^-$  also absorbs in the  $350\text{ m}\mu$  region of the spectra (see curve 4 of 1). The molar absorptivity of the product,  $\epsilon_p$ , cannot be accurately measured directly. There was probably decomposition of some of the product in the course of preparing the solution as evidenced by noticeable loss of NO from more concentrated solutions. This difficulty in measuring  $\epsilon_p$  can be circumvented by taking advantage of the isosbestic point for the product and nitric oxide at  $350\text{ m}\mu$  (Fig. 1). At this point  $\epsilon_{\text{NO}}$  equals  $1/2\epsilon_p$  and direct measurement of  $\epsilon_{\text{NO}}$  at this wave length in amine solution enables calculation of  $\epsilon_p$ . At  $350\text{ m}\mu$  a value of  $\epsilon_p$  equal to  $159 \pm 1$  is obtained. The

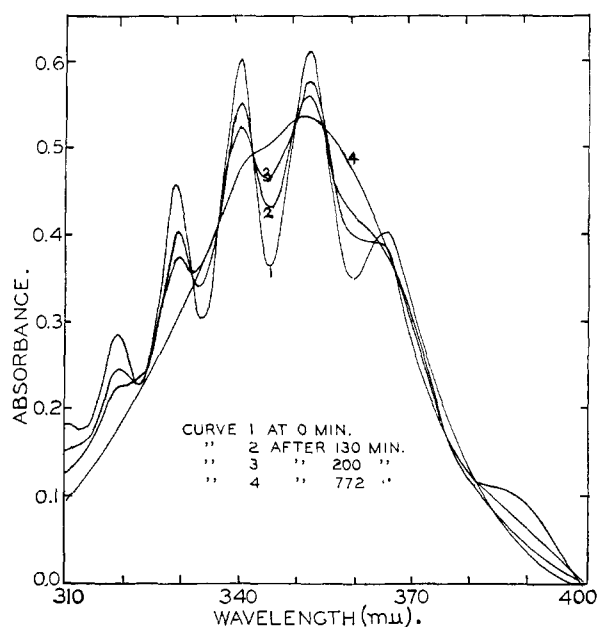


Fig. 1.—Spectra during the reaction of diethylamine (0.5 *M*) with nitric oxide in methanol solution at 35°.

product maximum is broad and by employing the spectrum obtained for the final reading in a kinetic run and comparing the absorbance values at 346 and 350  $\mu$ , it can be shown that  $\epsilon_p$  at 346  $\mu$  is  $157 \pm 1$  (l. mole<sup>-1</sup> cm.<sup>-1</sup>).

**Determination of the Nitric Oxide Concentration During Reaction.**—During the course of this reaction the greatest change in absorbance occurs at 346  $\mu$  (Fig. 1), so this wave length was employed to follow the reaction. The initial concentration of nitric oxide was obtained by utilizing the extrapolated value of the absorbance. This agreed with that calculated for dilution of the original nitric oxide solution by amine.

In order to calculate the nitric oxide concentration at any subsequent time, the absorption due to the product must be subtracted. At any time (*t*) during the reaction the total absorbance (*A*) at a fixed wave length is given by the expression

$$A = \epsilon_{NO}[NO]_t + \epsilon_p[P] \quad (7)$$

where [P] and [NO]<sub>*t*</sub> refers to molarity of product and nitric oxide, respectively, at time *t*;  $\epsilon_{NO}$  and  $\epsilon_p$  refer to the molar absorptivity of NO and product.

Since two moles of NO are involved in forming product, the following relation holds for the initial nitric oxide concentration [NO]<sub>*i*</sub>

$$[NO]_i = [NO]_t + 2[P] \quad (8)$$

Combining equations 7 and 8, eliminating [P] and solving for [NO]<sub>*t*</sub> one obtains

$$[NO]_t = \frac{2A - \epsilon_p[NO]_i}{2\epsilon_{NO} - \epsilon_p} \quad (9)$$

The measurement of all quantities on the right hand side has been described, and [NO]<sub>*t*</sub> at any time during the reaction can be calculated from the absorbance readings and equation 9.

### Results and Discussion

Table I contains the results (time and absorbance readings) and the values calculated for [NO]<sub>*t*</sub> for a typical experiment. All experiments were carried out in excess amine so the amine concentration was approximately constant during a given experiment.

Two mechanisms have been considered in detail, and these are represented by the two sets of equations 1, 2, 3 (referred to as I) and 4, 5, 6 (referred to as II). The steady state treatment<sup>4</sup> was ap-

plied to mechanism I assuming N<sub>2</sub>O<sub>2</sub> and Et<sub>2</sub>NHN<sub>2</sub>O<sub>2</sub> to be present in small steady state concentrations. It is assumed that step 3 involving proton transfer is a rapid one in methanol. The final expression for mechanism I is

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [Et_2NH][NO]^2}{k_{-1} + k_2 [Et_2NH]} \quad (10)$$

If step 1 is rate controlling  $k_{-1} < k_2 [Et_2NH]$  and equation 10 becomes  $\frac{d[P]}{dt} = k_1 [NO]^2$  (11). If step 2 is rate controlling  $k_{-1} > k_2 [Et_2NH]$  and

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [Et_2NH][NO]^2 \quad (12)$$

For mechanism II the steady state treatment is applied assuming that Et<sub>2</sub>NHNO and Et<sub>2</sub>NHN<sub>2</sub>O<sub>2</sub> are present in small steady state concentrations, thus

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [Et_2NH][NO]^2}{k_{-1} + k_2 [NO]} \quad (13)$$

If step 1 is the rate controlling step,  $k_{-1} < k_2 [NO]$  and equation 13 becomes

$$\frac{d[P]}{dt} = k_1 [Et_2NH][NO] \quad (14)$$

If step 2 is the rate controlling step  $k_{-1} > k_2 [NO]$  and equation 13 becomes

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [Et_2NH][NO]^2 \quad (15)$$

A kinetic study would provide evidence regarding the reaction mechanism and, if a first order dependence on nitric oxide were observed, a unique solution of the four mechanisms proposed would result [see equations 11, 12, 14, 15].

TABLE I<sup>a</sup>

KINETIC DATA FOR THE REACTION OF DIETHYLAMINE (0.5 *M*) WITH NITRIC OXIDE IN METHANOL AT 35°

Time, min.	Ab-sorbance	[NO] <sub><i>t</i></sub> × 10 <sup>3</sup> , mole/l.	Time, min.	Ab-sorbance	[NO] <sub><i>t</i></sub> × 10 <sup>3</sup> , mole/l.
0	0.350	6.48	132	0.420	3.63
2	.351	6.45	152	.426	3.30
4	.352	6.41	177	.436	2.78
11	.358	6.16	202	.443	2.69
21	.366	5.84	227	.449	2.45
36	.374	5.51	252	.456	2.16
51	.382	5.18	277	.461	1.96
71	.394	4.69	302	.465	1.80
91	.405	4.30	322	.469	1.63
112	.415	3.96			

<sup>a</sup> The precision of the absorbance readings is  $\pm 0.002$  resulting in a precision for [NO]<sub>*t*</sub> of about  $\pm 0.05$ .

The rate data obtained were applied to the integrated form of the rate expression. First and second order rate plots were attempted and a linear plot was obtained only for a first order plot, supporting a reaction mechanism first order in nitric oxide. The slope of the least squares line was calculated to obtain the rate constant  $k'$  which equals  $k[Et_2NH]^n$ . Since the reaction was carried out in excess amine,  $[Et_2NH]^n$  is essentially constant in any one experiment. Values for  $k'$  were obtained at 0.1 *M*, 0.5 *M* and 1.0 *M* amine

(4) S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 50-52.

concentrations. Various integers were substituted for  $n$  in the expression  $k' = k [\text{Et}_2\text{NH}]^n$  and  $k$  was calculated (see Table II). The constancy

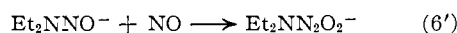
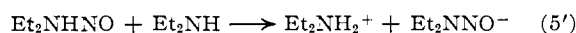
TABLE II<sup>a</sup>  
DETERMINATION OF THE ORDER OF DIETHYLAMINE

$[\text{Et}_2\text{NH}]_M$	$\frac{k'}{[\text{Et}_2\text{NH}]_n}$ ( $\text{min.}^{-1}$ )	Various values of $k$ ( $\text{min.}^{-1}$ )		
		$n = 1$	$n = 2$	$n = 1/2$
1.0	$4.05 \times 10^{-3}$	$4.05 \times 10^{-3}$	$4.05 \times 10^{-3}$	$4.05 \times 10^{-3}$
0.5	$2.48 \times 10^{-3}$	$4.96 \times 10^{-3}$	$9.9 \times 10^{-3}$	$3.51 \times 10^{-3}$
0.1	$5.14 \times 10^{-4}$	$5.14 \times 10^{-3}$	$51.4 \times 10^{-3}$	$1.61 \times 10^{-3}$

<sup>a</sup> Rate constants measured at 27°.

of  $k$  for  $n = 1$  supports a first order dependency of the rate on amine concentration. The resulting experimental rate expression  $d[\text{P}]/dt = k[\text{Et}_2\text{NH}][\text{NO}]$  is in support of the mechanism II where the first step (equation 4) is slow and rate controlling.

An alternate mechanism 5' and 6' is possible instead of steps 5 and 6. This involves removal of the proton from  $\text{Et}_2\text{NHNO}$  before attack by NO



This sequence of reactions cannot be positively ruled out but is regarded as less likely for trimethylamine reacts with nitric oxide to produce  $(\text{CH}_3)_3\text{NN}_2\text{O}_2$ . This result indicates that formation of an anion is not necessary for the NO dimerization step.

The order of the reaction calculated by the differential procedure from the data in Table I and also from other sets yielded values for  $n = 1.0$  to 1.2.

The rate constant for this reaction was measured in the temperature range 18.5 to 35° by assuming that  $\epsilon_p$  and  $\epsilon_{\text{NO}}$  have constant values over this temperature range. The results are contained in Table III. From these data a value of  $12.0 \pm 3.8$  kcal. mole<sup>-1</sup> is calculated for the activation energy. The error is estimated at the 90% confidence level.

TABLE III

TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

Temp., °C.	$[\text{Et}_2\text{NH}]$ , mole/l.	$k^a$
18.5	1.0	$2.3 \pm 0.2 \times 10^{-3}$
25	1.0	$4.2 \pm .2 \times 10^{-3}$
27	1.0	$4.05 \pm .2 \times 10^{-3}$
27	0.5	$4.96 \pm .2 \times 10^{-3}$
27	0.1	$5.1 \pm .2 \times 10^{-3}$
30	1.0	$4.4 \pm .2 \times 10^{-3}$
35	0.5	$8.8 \pm .2 \times 10^{-3}$
35	1.0	$7.8 \pm .2 \times 10^{-3}$

<sup>a</sup> Since the reaction is first order in  $\text{Et}_2\text{NH}$ , the  $k$  values can be calculated from  $k = k'/[\text{Et}_2\text{NH}]$ .

The kinetic data enable us to explain an interesting observation made in the synthesis<sup>1</sup> of the diethylammonium salt by the reaction of diethylamine and nitric oxide in ether at  $-78^\circ$ . Even though the product is insoluble and precipitates from solution, the yield realized is only 11%. Additional product could be obtained by further reaction of the filtrate, demonstrating that an inhibitor was not formed. Evidently the reaction is very slow at  $-78^\circ$ , and most of the product is obtained when the ether solution saturated at the low temperature is allowed to warm to room temperature in the work up. An increase in the amount of solid present in the reaction vessel is detected during the warm-up period. The yield obtained is determined by the amount of nitric oxide that has dissolved. When the reaction is carried out at room temperature, no compound is obtained. This probably is due to both the low solubility of nitric oxide in ether and the slow rate of absorption of nitric oxide in ether at room temperature. The product decomposes as fast as it is formed under these conditions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZONA]

## The Photolysis of Biacetyl Solutions<sup>1</sup>

BY STANLEY A. GREENBERG<sup>2</sup> AND LESLIE S. FORSTER

RECEIVED DECEMBER 8, 1960

Quantum yields of carbon monoxide, ethane and methane formation and biacetyl disappearance have been obtained for biacetyl dissolved in perfluoro-*n*-octane, FC-75, and mineral oil at 3660 and 4358 Å. as a function of concentration and temperature up to 100°. Only the mineral oil solutions were decomposed appreciably at 25°. In all solutions a 2nd order reaction between an excited biacetyl and an unexcited molecule occurs. In other respects, the 4358 Å. primary process is the same as that proposed by Sheats and Noyes. The carbon monoxide yield decreases markedly with biacetyl concentration at 3660 Å, but not at 4358 Å. The character of the reaction is therefore different at the two wave lengths. The primary process appears to be viscosity dependent at 3660 Å.

Although the gas-phase photochemistry of biacetyl has been the subject of numerous investi-

gations<sup>3</sup> and several reports on the luminescence of biacetyl solutions have appeared,<sup>4</sup> little infor-

(1) Based on a dissertation submitted by S. A. Greenberg in partial fulfillment of the requirements for the Ph.D. degree, University of Arizona. This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) National Science Foundation Cooperative Graduate Fellow, 1959-1960.

(3) (a) G. F. Sheats and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **77**, 1421, 4532 (1955). (b) W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956). (c) H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957).

(4) (a) L. S. Forster, S. A. Greenberg, R. J. Lyon and M. E. Smith, *Spectrochim. Acta*, **16**, 128 (1960). (b) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 3 (1958). (c) H. L. J. Backstrom and K. Sandros, *ibid.*, **14**, 48 (1960).