Tetrahedron, 1967, Vol. 23, pp. 965 to 984. Pergamon Press Ltd. Printed in Northern Ireland

KINETICS OF THE DECOMPOSITION OF A PHOSPHORYLATED TRIAZOLINE

EVIDENCE FOR A DIPOLAR ION INTERMEDIATE[1]

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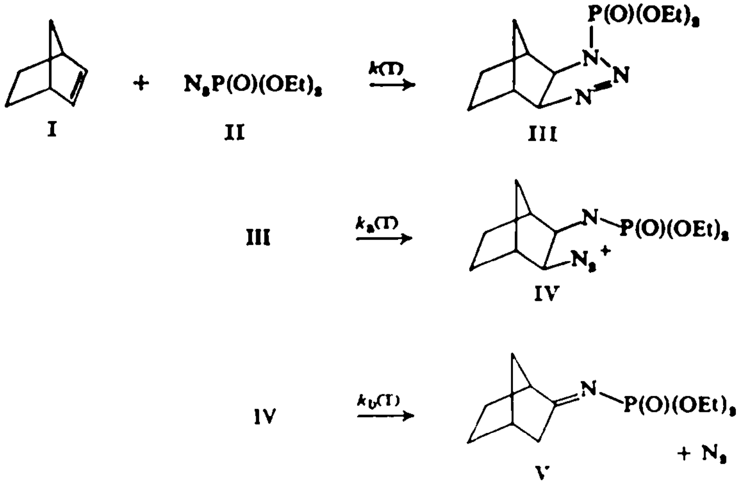
(*Received in U.S.A. 25 May 1966; accepted for publication 19 July 1966*)

Abstract—The formation of diethyl (3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-benzotriazol-1-yl)-phosphonate (III) from norbornylene and diethyl phosphorazidate (II) was studied kinetically and found to be second order overall. Decomposition of this phosphonate was carefully followed by the conventional technique of measurement of nitrogen loss and by differential thermal analysis (DTA). Two consecutive first order reactions were favored in the decomposition by the kinetic data. In the first step a dipolar ion IV is apparently formed which loses nitrogen in a second reaction to form a phosphorylated amidate V. Chemical as well as kinetic evidence supports the presence of a dipolar ion intermediate.

INTRODUCTION

IT has been proposed that the reaction of phosphorus azides and certain olefins, particularly norbornylene[1a] and dimethylisobutenylamine,[1b] proceeds via a 1,3-dipolar addition to form an intermediate triazoline. In the case of triazoline III, thermal decomposition occurs via a dipolar ion intermediate IV to give the phosphorylated amidate V. In the 1,3-dipolar additions of azides to olefins,[3] the triazoline adducts are suspect, and although stability of such adducts is extremely variable in many cases, the phenyl adduct of norbornylene has been synthesized.[3a]



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[1] For preliminary results see [a] K. D. Berlin and L. A. Wilson, *Chem. Commun.* 280 (1965); [b] *Ibid. Chem. & Ind.* 1522 (1965).

[2] Predoctoral candidate, 1963–1966.

[3] [a] G. Komppa and S. Beckman, *Liebigs Ann.* **512**, 172 (1934); [b] G. D. Buckley, *J. Chem. Soc.* 1850 (1954); [c] L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.* **28**, 3309 (1963); [d] P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.* **87**, 306 (1965).

Little work is published[4-6] that adequately demonstrates the presence of a dipolar intermediate in the decomposition of triazolines to form imines or aziridines. This study of the formation and decomposition of III offers considerable evidence for presence of IV. The decomposition appears to proceed via first order consecutive reactions as depicted in Eqs. 1–3.

Decomposition of the triazoline adduct of phenyl azide and I has been suggested to proceed through a dipolar ion intermediate from initial heterolytic N—N bond cleavage. Although no kinetic evidence for this ion was given it was possible to trap an intermediate with phenyl isocyanate.[6b] Certain olefinic azides have been postulated to yield a triazoline by intramolecular addition.[6c] Decomposition was stated to be first order and a dipolar ion intermediate was considered a strong possibility on the basis of product analysis. Huisgen has recently indicated the first-order decomposition in toluene at 85° of the triazoline from phenyl azide and methyl acrylate gave a high yield of the expected aziridine.[6d]

RESULTS

Structure of triazoline III *and amidate* V. The chemical and physical evidence for the structure of the compounds examined was only briefly outlined in a preliminary communication.[1a] The structure of III is based primarily on NMR evidence and on the decomposition to V with stoichiometric loss of nitrogen. The NMR shows an AB quartet centered at $\delta 4{\cdot}10$ ($J = 8{\cdot}5$ c/s) which has been assigned to the C-3α, C-7α bridgehead protons, that do not appear in the product V formed by the loss of one mole of nitrogen. The structure of V is based on chemical evidence and its NMR and IR spectra. Amidate V was hydrolyzed in both acid and base to give norcamphor which was recovered in 85% yield as its 2,4-dinitrophenylhydrazone along with ammonia, ethanol and phosphoric acid. The IR spectrum of V shows no N—H absorption in the 3 μ region and no bands characteristic of carbon–carbon double bonds. There is strong absorption for C=N at $5{\cdot}98$ μ. The NMR spectrum contains peaks for the nonequivalent C-4, C-7 bridgehead protons at $\delta\, 2{\cdot}5$ and $2{\cdot}65$, respectively. Similarly, a doublet is observed ($\delta\, 2{\cdot}85$ and $3{\cdot}10$) in the 2,4-DNP of norcamphor, a close model compound in the same solvent. The fact that V was obtained from III in yield greater than 95% also lends strong support to the structure of III.

Kinetics of decomposition of triazoline as followed by nitrogen evolution. The rate of formation of products at various temperatures was followed by measuring the amount of nitrogen evolved at specific times during the decomposition of III. The apparatus shown in Fig. 1 is described in the Experimental. The kinetics were determined by attempting to fit the various rate laws with the data obtained. The data is consistent with first order consecutive reactions as depicted in Eqs. 1–3. The data does not fit well for simple systems that could be proposed (Figs. 2–5).

Note that the first order plot (Fig. 3) in diglyme is not linear. The deviation is greatest toward the end of the reaction and is a positive deviation. This type of behavior is characteristic when the presence of the intermediate always results in

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[4] R. Fusco, G. Bianchetti, D. Pocar and R. Ugo, *Chem. Ber.* **96**, 802 (1964).

[5] F. D. March and M. E. Hermes, *J. Amer. Chem. Soc.*, **86**, 4506 (1964).

[6] [a] R. Huisgen, *Angew. Chem.* (Int. Ed.) **2**, 633 (1963); [b] J. E. Baldwin, G. V. Kaiser and J. A. Romersberger, *J. Amer. Chem. Soc.* **87**, 4114 (1965); [c] A. L. Logothetis, *J. Amer. Chem. Soc.* **87**, 749 (1965); [d] G. Szeimies and R. Huisgen, *Chem. Ber.* **99**, 491 (1966).

such deviation in a logarithmic plot assuming a first order dependence. Stated in another way the nitrogen lost is less than expected, a situation which can be explained by consecutive first order reactions. A plot of $[N_2]$, [III] and [IV] is provided (Figure 6 data provided from the run in diglyme at 391·2°K). A least squares procedure was employed to evaluate the first order k given by $\ln A_0 - \ln (A_0 - N_2) = kt$. The deviation is given in Table 1. With the best value of k, a measure of the preciseness of the fit was obtained by calculating the root mean square deviation of the points from the experimental line, R (Fig. 3). The value of R is defined as

$$R = \left[\sum_{i=1}^{N} (Y_i^c - Y_i^e)^2/N\right]^{1/2} = [S_{min}/N]^{1/2} \tag{4}$$

where Y_i^c = calculated ith point, Y_i^e = experimental ith point $= \ln [A_0 - N_2^e]_i$ where N_2^e = experimentally measured nitrogen in moles, S = sum of the squares and N = total number of points available. Values for the first order k and R are found for each set of data in Table 1.

The rate constants (k_a and k_b) were calculated by means of the following equations.[7] For convenience and simplification of the equations, let

A_0 = concentration of triazoline initially
A = concentration of triazoline at time t
B_0 = concentration of dipolar intermediate initially
B = concentration of dipolar intermediate at time t
P = concentration of amidate at time t
C = concentration of nitrogen at time t
C_0 = concentration of nitrogen initially

Then for the reaction:

$$A \rightarrow B$$
$$B \rightarrow C + P$$

we have

$$\frac{dA}{dt} = -k_aA \tag{5}$$

$$\frac{dB}{dt} = k_aA - k_bB \tag{6}$$

$$\frac{dC}{dt} = k_bB \tag{7}$$

Solution of these equations by conventional techniques[7] using as the initial conditions, $B_0 = C_0 = 0$ and the stoichiometry, we have the following equations.

$$A + B + C = \text{constant} = A_0 + B_0 + C_0 = A_0 \tag{8}$$

$$C = A_0 - (A + B)$$

$$A = A_0e^{-k_at} \text{ (from simple first order kinetic considerations)}$$

$$B = B_0e^{-k_bt} + \frac{k_aA_0}{k_b - k_a}\left[[e^{-k_at} - e^{-k_bt}\right]$$

$$C = A_0 + B_0 + C_0 - A_0e^{-k_at} - B_0e^{-k_bt} - k_aA_0/(k_b - k_a)[(e^{-k_at} - e^{-k_at})]$$

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[7] For a complete description of this type of system see S. W. Benson, *The Foundation of Chemical Kinetics*, p. 33. McGraw-Hill, New York, N.Y. (1960).

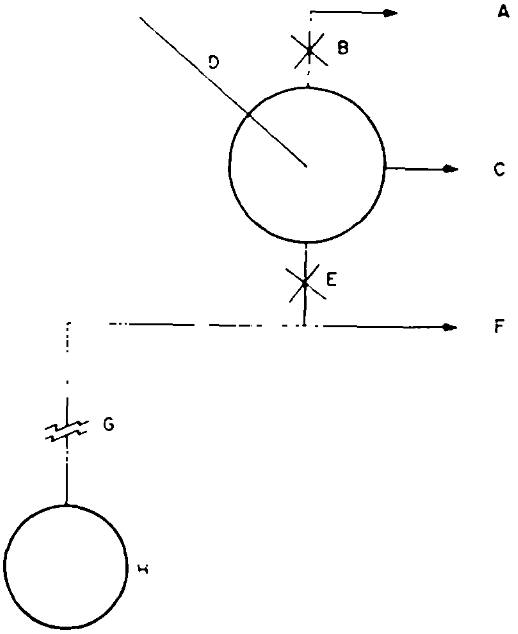

Fig. 1. Apparatus for measurement of N_2 evolved by conventional method: A, to vacuum pump; B, stopcock; C, to manometer to measure N_2 pressure; D, evacuated bulb with thermometer; E, stopcock to allow N_2 produced to enter D; F, to manometer to monitor reaction system pressure; G, condenser; H, reaction flask.

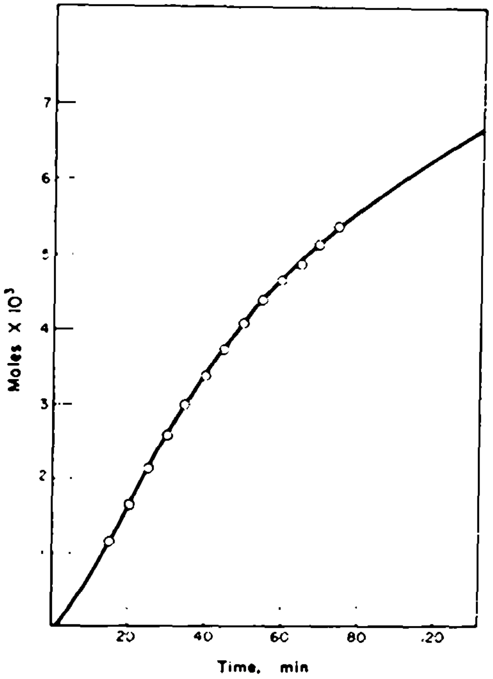

Fig. 2. Plot for the formation of nitrogen in diglyme at 381·2° K., assuming zero order reaction.

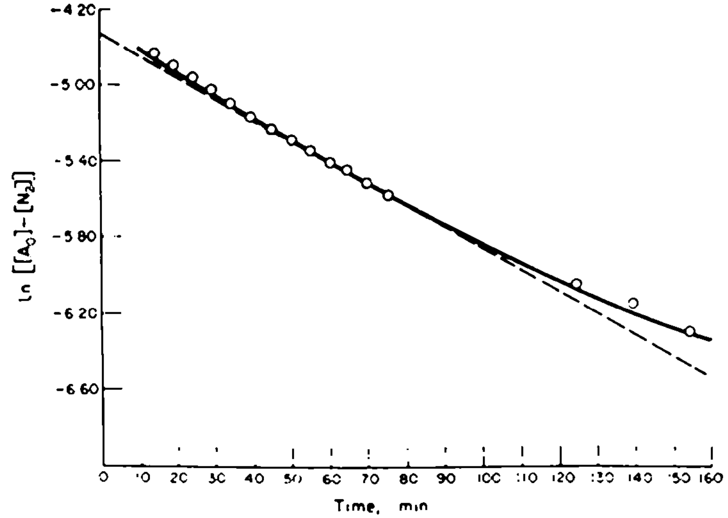

FIG. 3. Plot for the formation of N_2 in diglyme at 381·26° K. assuming a simple first order reaction.

——— Curve of experimental data

- - - - - Least squares plot of data

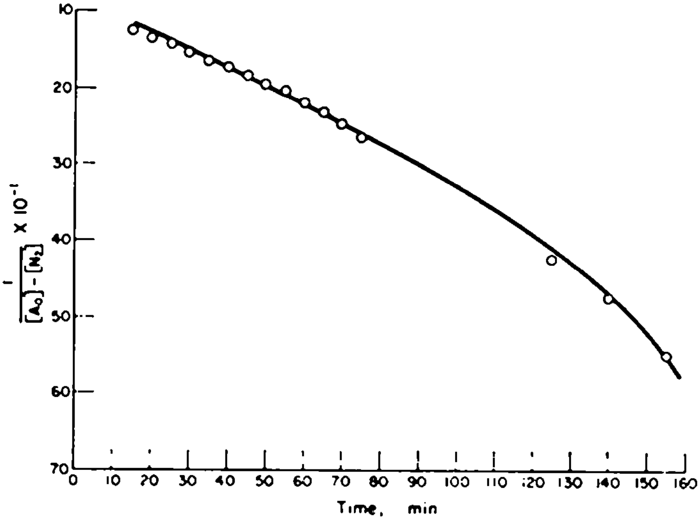

FIG. 4. Plot for formation of N_2 in diglyme at 381·26° K. assuming a simple second order reaction.

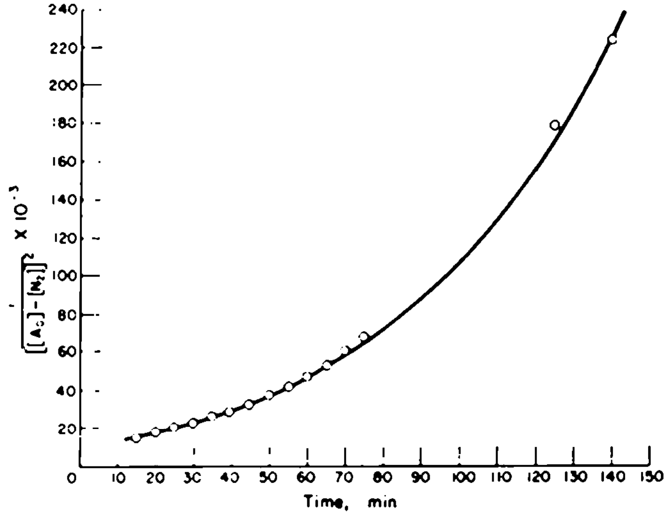

Fig. 5. Plot for the formation of N_2 in diglyme at 381·26° K. assuming a simple third order reaction.

Table 1. Rate constants and R values for decomposition of III in diglyme

Temp °K	1st Order k	R × 10^3	k_a	k_b	R × 10^3
371·2	0·004678	0·10857	0·005431	0·06138	0·014976
380·9	0·01034	0·07287	0·01161	0·1936	0·01706
391·2	0·04208	0·28927	0·04598	0·1628	0·060102
399·7	0·08073	0·2025	0·09777	0·2240	0·05365

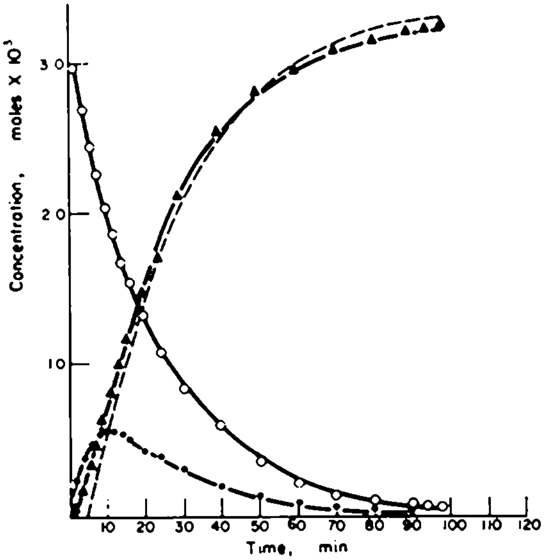

Fig. 6. Plot of calculated concentrations of [III], [N_2] and [IV] as a function of time at 391·2° K. in diglyme. - - - Experimental N_2 curve; ▲ calculated N_2 curve; ○ calculated [III] curve; ● calculated [IV].

TABLE 2. COMPARISON OF CHANGES IN CONCENTRATIONS OF CALCULATED VALUES FOR III, IV, AND NITROGEN WITH TIME AT 391·2°K. IN DIGLYME, k_a = 0·04598, k_b = 0·1628

Time (min)	moles × 10^4		
	Nitrogen	III	IV
0	0·000	32·620	0·000
2·00	0·425	29·754	2·440
4·00	1·492	27·139	3·987
6·00	2·954	24·755	4·909
8·00	4·642	22·580	5·396
10·00	6·437	20·596	5·586
14·00	10·053	17·136	5·430
16·00	11·785	15·633	5·203
20·00	14·991	13·004	4·623
24·00	17·799	10·820	4·000
30·00	21·273	8·211	3·134
40·00	25·413	5·184	2·021
50·00	28·061	3·273	1·284
60·00	29·740	2·067	0·812
70·00	30·801	1·305	0·513
80·00	31·471	0·824	0·324
90·00	31·894	0·520	0·204
94·00	32·016	0·432	0·170
98·00	32·118	0·360	0·141

But $B_0 = C_0 = 0$. So, eliminating B_0 and C_0 and rearranging we have

$$C/A_0 = 1 - e^{-k_a t} - k_a/(k_b - k_a)[(e^{-k_a t} - e^{-k_b t})] \tag{9}$$

In this case the complexity of Eq. 9 prevents any simple plot from yielding a straight line from which the "best" values of k_a and k_b can be obtained. If we assume k_a is less than 0·1 k_b, Eq. 9 reduces to

$$(1 - C/A_0) = e^{-k_a t}[1 + k_a/(k_b - k_a)] \tag{10}$$

which can be solved simultaneously at $t = t_1$, $t = t_2$ and $C = C_1$, $C = C_2$ to give

$$k_a = 1/(t_2 - t_1) \ln [(1 - C_2/A_0)/(1 - C_1/A_0)] \tag{11}$$

Similar assumptions and solution of Eq. 9 simultaneously at two concentrations corresponding to two times for k_b, gives

$$k_b = [k_a/(1 - C/A_0)(e^{k_a t}) - 1] + k_a \tag{12}$$

Solution of these equations for k_a and k_b was accomplished on an IBM 1410 digital computer by obtaining an initial value for k_a from eq. 11 and k_b from Eq. 12 for each set of 15 points. These approximate values for k_a and k_b were then used to provide the initial values in the more exact analysis described below.

One now wishes to perform an analysis comparable to that carried out for the first order case so that a direct comparison of results is possible. Thus one still wishes to minimize the S of Eq. 4 with respect to the rate constant, k_a and k_b. Thus in principle one would obtain two equations for the minimization condition

$$\partial S/\partial k_a = 0 \qquad \text{and} \qquad \partial S/\partial k_b = 0$$

and solve these two equations for the "best" values of k_a and k_b. Unfortunately, the equations produced from these two equations are too complex to admit of easy solution, even on a computer. Therefore, an alternate technique was adopted. This technique is described on the following page:

An initial value for k_a was chosen from the values obtained via the first order analysis with k_b being taken to be ten times the k_a value. Using these values, the value of R given by Eq. 4 was calculated with Y_i^c given by Eq. 9. Following this calculation, the value of k_b was altered slightly and a new value of R calculated. This procedure was then repeated until ten values of k_b spanning a rather large range had been used. At this point a new value of k_a was chosen, and the value of k_b reset to its initial value. A new R was calculated, and then the entire range of k_b values was again scanned. This procedure was repeated until ten values of k_a had been examined with each possible value of k_b, making 100 values of R calculated in all. The range of k_a values tested also spanned a rather large range. After all 100 values of R had been calculated, they were examined on an IBM 7040 computer, and the smallest value of R corresponding to the best fit of k_a and k_b values was located. The entire procedure was then repeated using these k_a and k_b values as the initial values with the range of scanning reduced by a factor of 5. This overall procedure of finding the smallest value of R and then using the corresponding k values as initial values in the scanning of a smaller 100 fold grid was repeated five times so that the final result is a value of R for k_a and k_b values which minimize the value of S to about four significant digits. This procedure is entirely equivalent to that performed for the simple first order case, and the values of R obtained can be directly compared. The smaller values correspond to the better fits.

Many runs were made in which the nitrogen evolution was followed carefully as a function of time at one temperature to check accuracy of measurement. Values for k_a and k_b are given in Table 1 at various temperatures. Table 3 contains data for the points obtained by the least squares analysis needed to calculate the thermodynamic quantities. Figures 7 and 8 are Arrhenius plots of these data. Figure 7 also includes data from the DTA analysis described below.

Solvent dependence of the rate constants k_a *and* k_b. A study of the effect of increasing solvent polarity on the rate of decomposition of III indicates that there is indeed a considerable increase in the reaction rate as the solvent polarity is increased. Because k_b in toluene is so large compared to k_a, it was only possible to set a lower limit on the former (see Table 4).

Kinetics of the decomposition of III *determined by* DTA. The DTA curves obtained from the decomposition of triazoline III were analyzed by the method published.[8] Only a first order reaction gives the best fit of the data. The values of the rate constants obtained, listed in Table 5, agree with the results for this rate constant as determined by following the rate of formation of nitrogen (Fig. 7).

The approximations that the heat capacity (C_p) term and the cell constant (K) term in the equation (Eq. 13),[8] are insignificant within the experimental error were

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[8] H. J. Borchardt and F. Daniels, *J. Amer. Chem. Soc.* **79**, 41 (1957).

tested by including them in a sample calculation. Such approximations were found to make very little difference in the rate constants obtained. Thus the Borchardt and

$$k = \left[\frac{KAV}{n_0}\right]^{x-1} \frac{C_p \frac{d\,\Delta T}{dt} + K\,\Delta T}{[K(A-a) - C_p\,\Delta T]^x} \tag{13}$$

Where: A is total area under the DTA curve; a is the area under the curve of time t; K is the cell constant; V is the volume of the material charged; n_0 is the initial concentration; C_p is the heat capacity of the sample and reference which are assumed to be about the same; ΔT is the height of the DTA curve at time t; $d\,\Delta T/dt$ is the slope of the DTA curve at time t; and x is the reaction order.

Daniels equation reduces to the very simple equation

$$k = [(KAV/n_0)^{x-1}]K\,\Delta T/[K(A-a)]^x \tag{14}$$

which for first order reactions (x = 1), reduces still further to give:

$$k = \Delta T/(A-a) \tag{15}$$

TABLE 3. RATE CONSTANT DATA FOR CALCULATION OF THERMODYNAMIC QUANTITIES

Temp °K	ln k_a	ln k_b	$10^3/T$
371·2	−5·2158	−2·7904	2·69
380·9	−4·4556	−1·6160	2·62
391·2	−3·0791	−1·814	2·55
399·7	−2·3248	−1·4110	2·50

E_a = 30·93 kcal/mole	E_a = 14·04 kcal/mole
A = 7·92 × 10^{16} min^{-1}	A = 1·16 × 10^{7} min^{-1}
A = 13·2 × 10^{14} sec^{-1}	A = 19·3 × 10^{4} sec^{-1}
ΔS^{*}(391·2°K) = 5·53 cal/mole-degree	ΔS^{*}(391·2°K) = −34·9 cal/mole-degree

The method itself was checked by running a DTA curve for the reaction of N,N-dimethylaniline and ethyl iodide. The ratio of reactants and conditions were the same as those employed by Borchardt and Daniels except for the small cells and fact that the cells were not stirred. The results in Fig. 9 show very close agreement with the data published.[9,10]

Kinetics of the formation of III *from azide* II *and norbornylene.* The formation of triazoline III was studied by following the rate of formation of triazoline by ultraviolet spectroscopy and by following the rate of disappearance of norbornylene by NMR. The data obtained indicate that the reaction is simple second order over all and first order in norbornylene (Experimental). The results are given in Table 6. Activation energies and entropies of activation calculated from the Arrhenius equation and from transition state theory, respectively, are included in the Tables.

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[9] See Ref. 8 and S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*. McGraw-Hill, New York, N.Y. (1941).

[10] E. A. Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, p. 42. Oxford Univ. Press, (1933).

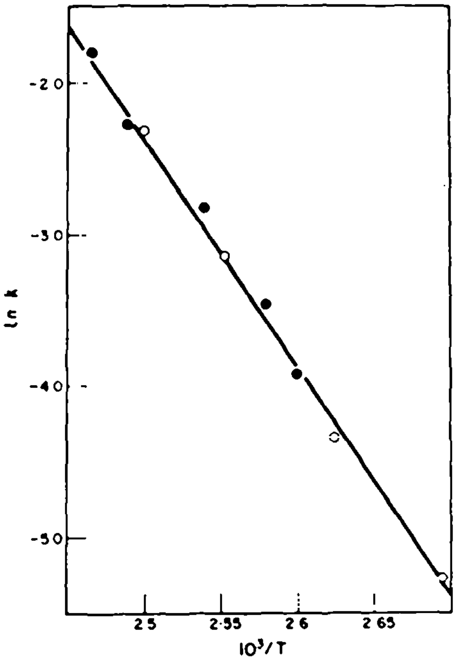

FIG. 7. Arrhenius plot for the first order decomposition of III; ○ are data obtained by conventional method of N_2 evolution; ● are data obtained by DTA.

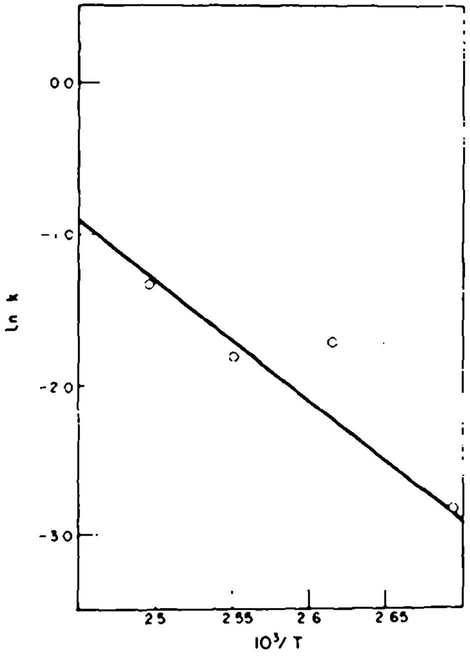

FIG. 8. Arrhenius plot of the first order decomposition of the dipolar ion intermediate by conventional method of N_2 evolution.

TABLE 4. SOLVENT DEPENDENCE OF RATE CONSTANTS AT 381·0 ± 0·1°K

Solvent	10^2k_a(min^{-1})	$10k_b$(min^{-1})
Toluene	0·576	1·5
Diglyme	1·161	1·93
Benzonitrile	2·85	2·92

TABLE 5. RATE CONSTANTS FOR TRIAZOLINE DECOMPOSITION BY DTA

Temperature °K	$10k_a'$(min^{-1})
383·4	0·1984
387·0	0·3186
390·4	0·4365
394·0	0·6063
397·5	0·8148
400·9	1·1543
404·0	1·6587
407·2	2·076
410·2	2·585
413·5	3·390
416·2	4·287
419·5	5·238
422·6	6·063
425·4	6·499

E_a = 29·0 kcal/mole

TABLE 6. REACTION OF NORBORNYLENE WITH DIETHYL PHOSPHORAZIDATE

Temp ± 0·02°C	10^4 k(l./mole-min)
34·90	3·66
30·00	1·95
25·00	1·52
25·00	1·52

E_a = 15·3 kcal/mole
ΔS^* = −27·4 cal/mole-degree

Decomposition of III. Figures 2, 3, 4 and 5 clearly show the reaction does not follow simple zero, first, second, or third order rate laws. Figs. 10 and 11 demonstrate that the disappearance of III is apparent first order. If the data are assumed to be consistent with first order consecutive reactions (Eqs. 2 and 3), the root mean square deviation (R of Eq. 4) is smaller by factors of 4 to 8 than the deviation values obtained with an assumed first order rate (Table 1). Table 2 (plot in Fig. 6) shows a comparison of change in concentrations of III, IV and nitrogen. The concentration of IV was determined by calculating the concentration of N_2 (C) at time t from the calculated values of k_a and k_b by Eq. 9. Since $A = A_0e^{-k_at}$ (and A = III), IV could

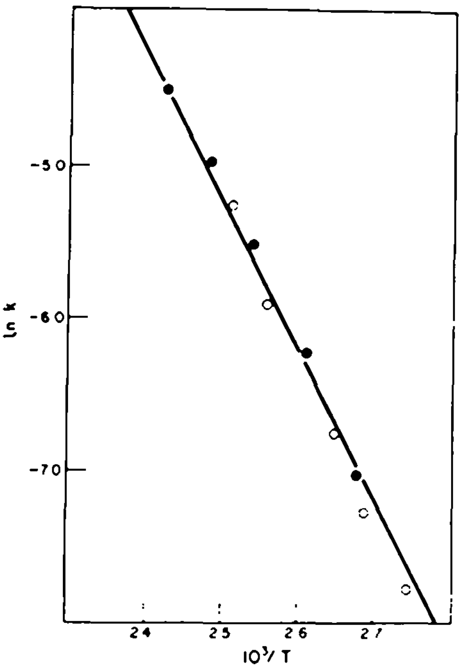

FIG. 9. Arrhenius plot for the reaction of N,N-dimethylaniline with ethyl iodide. Solid line are data by Moelwyn-Hughes,[10] ○ are data by Borchardt and Daniels,[8] ● are data obtained in the present work.

be calculated from Eq. 8.[11a] The concentration of IV is much less than the concentration of III during the reaction in diglyme at 391·2°K. (See Table 2.) The question of an equilibrium between III and IV is logical and the following considerations are directed thereto. Thus if

$$A \underset{k_r}{\overset{k_a}{\rightleftharpoons}} B$$

$$B \xrightarrow{k_b} C$$

rather than

$$A \xrightarrow{k_a} B$$

$$B \xrightarrow{k_b} C$$

then $dA/dt = -k_a[A] + k_b[B]$ and $dA/dt = -k_a[A]$ should not hold. First of all, the first order plots of ln [III] versus time (Figs. 10 and 11) show a linear[11c] relationship which would not be expected if k_r were large or if $dA/dt = -k_a[A]$ did not hold. As an additional check for any equilibrium process in which steady state conditions would exist (since [IV] is low), $d[N_2]/dt$ (slopes were obtained from Fig. 2 by numerical differentiation technique) was plotted against [III].[11b] The data did not give a straight

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[11] [a] The gradient method of Moore was also used to calculate IV but the method is tedious and no more accurate than the method actually used, see J. P. Hoare, *J. Chem. Ed.* **38**, 570 (1961); [b] see Ref. 15, p. 195, Eq. 103; [c] The basic techniques for these determinations are available; see Ref. 3*d*.

line (Fig. 12, data in Table 7) which would be required if k_r were significant in the equilibrium III $\underset{k_r}{\overset{k_a}{\rightleftharpoons}}$ IV since the following relationships would be valid,

$$d[N_2]/dt = k_bB$$

$$d[IV]/dt = k_a[A] - k_r[B] - k_b[B]$$

At steady state, $d[IV]/dt = 0$ and $[IV] = [B]$ and $[III] = [A]$, so $[IV] = k_a/(k_b + k_r)$ $[III]$. Thus $d[N_2]/dt = k_ak_b/(k_b + k_r)[A] = k'[A]$.

In any case the necessary steady state condition, $d(IV)/dt = 0$, is indeed a poor one at the higher temperatures as can clearly be seen from Figure 6.

EXPERIMENTAL[12]

Preparation of diethyl phosphorazidate. In the method used for the preparation of diethyl phosphorazidate (II),[13] the yield was improved considerably (nearly quantitative) by using purified reagents and by keeping the reactants under N during the preparation and purification, b.p. 71° (2·5 mm), $n_D^{24} = 1{\cdot}4283$; reported[13] b.p. 76° (4·5 mm), n_D^{20} 1·4620.

Preparation of triazoline for decomposition studies. Diethyl (3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate was obtained in high yield by allowing 10·0 g (0·056 mole) diethyl phosphorazidate and 20·0 g (0·212 mole) norbornylene to react at 45° for 40 hr. The extent of reaction was determined by following the azide absorption in the 4·7 μ region in the IR. Triazoline (13·9 g, 91·6%) was obtained after removing unreacted azide and norbornylene *in vacuo* at 45° (0·2 mm). IR analysis of the material indicated the absence of unreacted azide and also of any decomposition products as evidenced by the lack of absorption at or near 6 μ.

Preparation of diethyl2-norbornylidenephosphoramidate (V). Phosphoramidate V was prepared by first allowing 10 g (0·056 mole) of II to react with excess norbornylene (13·2 g, 0·140 mole) for about 50 hr at 40–46° and then adding 50 ml toluene and heating at reflux to decompose the triazoline. Nitrogen (1·25 l.) was collected over water (calc. 1·26 l.). The solvent was removed *in vacuo* and the product distilled to obtain 12·1 g (86·2%), b.p. 119° (2·0 mm). (Found C, 54·43; H, 8·43; N, 5·98; P, 12·63. Calc. for $C_{11}H_{20}NPO_3$: C, 53·57; H, 8·22; N, 5·71; P, 12·63%.)

Measurements of rate constants for the decomposition of the triazoline

I. *By measurement of nitrogen gas evolution.* Apparatus for the measurement of N evolved is shown in Fig. 1. A typical run is as follows. Xylene (50 ml) was placed in the reaction flask and the soln was allowed to equilibrate at 107·8 ± 0·1° for 15 min. During this time, the entire system was flushed 2 to 5 times with dry N. Triazoline (2·70 g, 0·099 mole) was then added quickly to the system which was then sealed. The press on the system was maintained at about 0·0 mm by allowing the N to escape through the stopcock (E) into an evacuated bulb (D). N press was measured at time *t* by closing the leak at time *t* and observing the press in the evacuated bulb. The release of N was then initiated again to maintain zero press on the system until the next reading was made. The press was estimated to 0·5 mm ± 0·2 mm. The number of moles of N evolved were calculated from the ideal gas law using the appropriate constants (volume of the bulb and temp in the bulb) for the system. The run was terminated when the extent of reaction reached 0·80 to 0·90. The initial concentration of triazoline was then checked by either increasing the temp to speed the reaction to completion or by simply waiting until gas evolution has ceased and measuring the total gas evolved. In most runs these two values agreed very closely. If the values did not agree closely, the initial concentration was calculated from the total N evolved using the volume of the evacuated bulb (D) assuming an ideal gas.

II. *By differential thermal analysis.*[14] The apparatus used to study the decomposition of the triazoline is shown schematically in Fig. 13.

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[12] IR spectra were obtained with a Beckman IR-5A IR spectrometer. NMR spectra were obtained with a Varian Model A-60 spectrometer using CCl_4 as solvent with TMS as internal standard. Elemental analyses were done by Galbraith Laboratories Inc., Knoxville, Tenn.

[13] F. L. Scott, R. Riordcn and P. D. Martin, *J. Org. Chem.* **27**, 4255 (1962).

[14] See Ref. 9 and W. M. Wendlandt, *Thermal Methods of Analysis*, Vol. 19 in the series, *Chemical Analysis*, p. 132–271. Interscience, New York, N.Y.

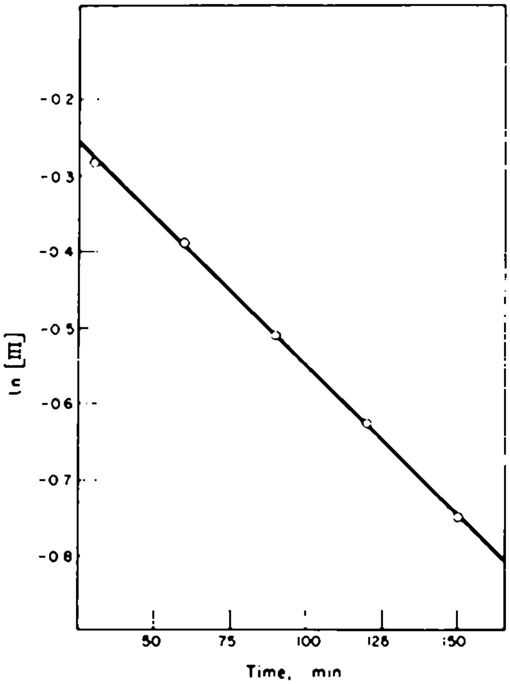

Fig. 10. First order plot for the decomposition of III in xylene at 381·6°K. as followed by NMR.

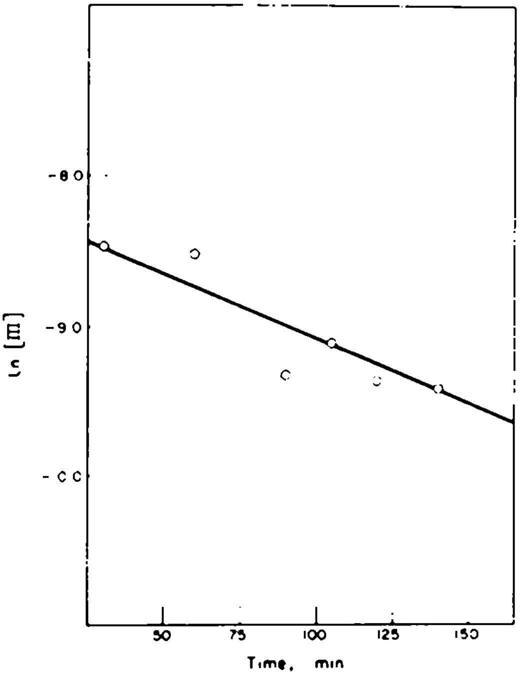

Fig. 11. First order plot for the decomposition of III in diglyme at 383°K. as followed by absorption in the ultraviolet at 240 mμ.

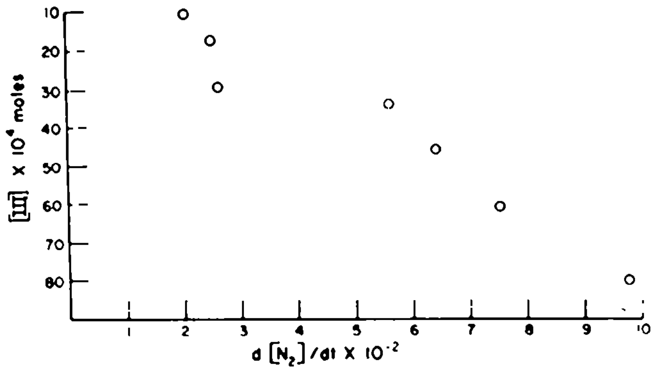

FIG. 12. Plot of change in concentration of N_2 versus [III].

TABLE 7. DATA FOR FIGURE 12

$d[N_2]/dt \times 10^{-2}$	[III] $\times 10^4$ moles	Time (min)
9·858	80·0	10
7·583	60·5	30
6·349	45·5	50
5·767	34·5	70
2·599	30·0	80
2·529	17·0	120
2·020	11·5	155

The sample cells were made of thin wall soft glass tubing with round bottoms 0·275″ in diameter (snug fit in the copper block) by 1·0″ long. The chromel-alumel differential thermocouple (DTC) (0·012″ T.C. wire) was enclosed in soft glass and centered in the cell by means of a one hole cork stopper. The cell holder consisted of a 1·50″ by 2·0″ high Cu cylinder, with the proper holes drilled for the sample and reference cells and the thermocouple to measure the temp of the block. Nearly linear rates of heating, namely, 3, 4 and 5 degrees/min, were obtained over the range 90–150° by simply placing the block in a heating mantle filled with sand and applying a constant voltage by means of a variac to the heating mantle.

The potential change was recorded on a Heath Company strip chart recorder after amplification with the D.C. amplifier at a chart speed of 2″/min. The amplifier and recorder were calibrated by applying a known potential from a Minneapolis-Honeywell (Rubicon) potentiometer to the input of the amplifier at different settings on the sensitivity (gain) and noting the pen deflection of the recorder.

The DTA curve obtained was then transferred to smaller paper for convenience in measuring the areas necessary for the calculation of rate data. At the same time the chart paper units (m.v). were converted to units of temperature so that the rate constants calculated had the proper units (min^{-1}) for a first order reaction.

A typical run is as follows: triazoline III (0·1094 g, 0·004 mole) and 0·2885 g diglyme were charged to the DTA cell and placed in the block. A reference cell containing an equiv amount of either silica gel or diglyme was placed in the other hole in the block. The DTC was carefully centered in the sample material and reference material, and the block was enclosed in a glass cylinder filled with glass wool to insulate and protect the cell and block from air currents. The block was then heated in a sand bath as described above. The temp of the block was estimated to ±0·1° at 30 sec intervals during the run with a Leeds and Northrop temp potentiometer, compensated for an iron-constantan thermocouple. The DTA curve was obtained in about 22–25 min at a heating rate of 3°/min. Figure 14 is the curve obtained after the original tracing had been transferred to a smaller scale. The maximum in the curve occurs at 134·9°. The enthalpy for the reaction was determined by running a DTA curve for the fusion of a 0·1527 g sample of *o*-toluic acid immediately following the DTA run on triazoline.

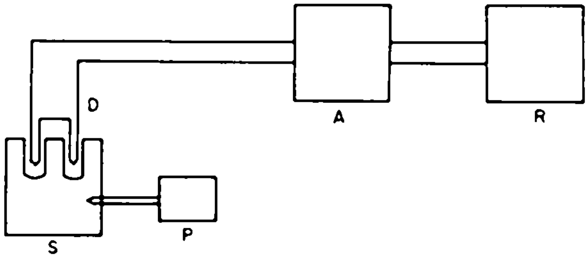

Fig. 13. DTA apparatus: S, sample block; P, temperature potentiometer with thermocouple; D, chromel-alumel DTC; A, d.c. amplifier; R, strip-chart recorder.

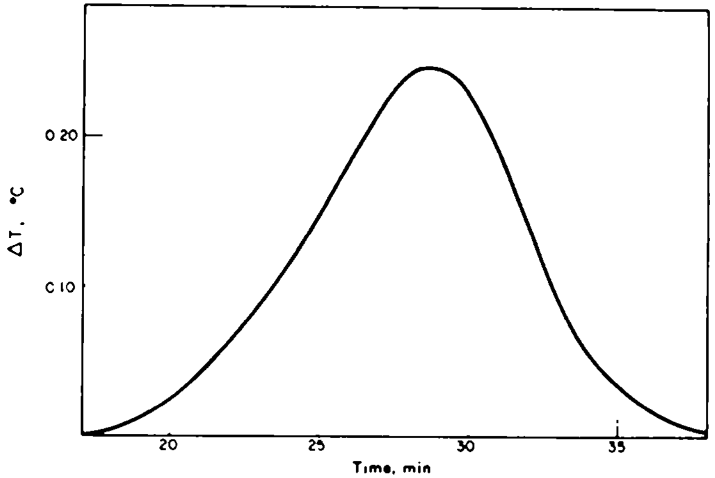

Fig. 14. Tracing of TDA curve.

The area obtained was 23·88 sq. in. (measured with a Keuffel & Esser compensating polar planimeter). Using the known heat of fusion for *o*-toluic acid (35·4 cal/g), this corresponds to 0·175 cal/sq. in. The DTA curve from the triazoline gave an area of 37·00 sq. in., which corresponds to an enthalpy of reaction of −16·2 kcal/mole (Fig. 14).

Kinetics of the formation of triazoline III. The rate constant as a function of temp for the formation of III from I and II was determined by the method of initial rates.[15] The procedure employed was similar to that described[14] to determine the rate constants for the formation of triazolines from norbornylene and substituted phenyl azides. For example, standard solns of 1·949 molar azide and 6·937 molar norbornylene in cyclohexane were prepared and allowed to equilibrate in a constant temp bath at 25·00 ± 0·002° for about 30 min. A 1 ml sample of the azide and a 3 ml sample of norbornylene soln were mixed in a tightly stoppered 3 ml (1 cm) quartz cuvette. The reaction mixture was then placed in the sample beam of a Cary 14 spectrophotometer. A 3 ml sample containing 1 ml of the azide soln in cyclohexane was used in the reference beam. The reaction was then examined periodically at 271·7 mμ where the molar extinction coefficient for the azide was less then 10. After about 100 min the change in absorbance was about 1·0 units, corresponding to an extent of reaction of nearly 0·01. The slope of the straight line observed, Δ absorbance/Δ time, was related to the reaction rate, $d(\mathrm{III})/dt$, by multiplying the latter by ε^{-1}. The rate constant (k) was calculated from the initial concentrations of I and II. The order of the reaction with[16] respect to norbornylene was calculated by the method of initial rates to be 1·04 (approximately 1 within experimental error) by varying the initial concentration of II and measuring the reaction rate.

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[15] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, p. 45. Wiley, New York, N.Y.

[16] See Ref. 15 and W. W. Wendlandt, *J. Chem. Ed.* **38**, 571 (1961).

The overall order was obtained in a separate study from the integrated second order rate equation by the use of NMR as follows. Norbornylene (0·9864 g, 0·0105 mole), 0·2616 g (0·00335 mole) benzene and 2·1211 g (0·01183 mole) of II were mixed in a 10 ml volumetric flask and diluted to volume. A small sample was then placed in an NMR sample tube in a thermostated bath at 311·3°K. The extent of reaction was followed by observing the disappearance of norbornylene, relative to the internal standard benzene, in the NMR as a function of time. The rate constant, calculated at the different times, gave a good fit for second order reaction, $k(311{\cdot}3°K) = 1{\cdot}96 \times 10^{-3}$ liters/mole-hr.

DISCUSSION

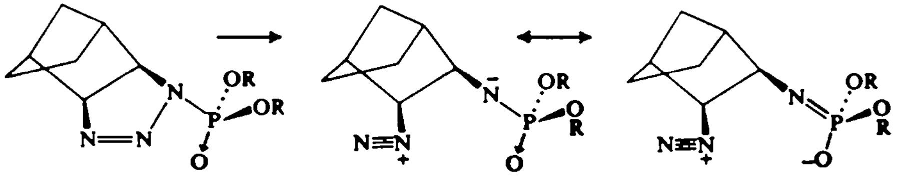
DTA analysis. The utility of DTA to the metallurgist, the inorganic chemist, and the analytical chemist is well known though its full potential even in these areas has not been realized. When knowledge of a reaction mechanism is desired via kinetics. DTA can be an invaluable tool due to the ease with which measurements can be made and the simplicity of the method. The only requirements for a reaction are that: it be endo- or exothermic, it be slow enough at some low temperature that is reasonable, the measurements can be made at the onset of the reaction when reactants are mixed, and it be fast enough that the process goes to nearly completion during the run in a reasonable length of time. It is obvious that these very broad requirements are also markedly dependent upon the sophistication of the equipment employed.

These prerequisites are met to a certain degree in the reaction studied here by this method. The decomposition rate of III is very slow at room temperature. In fact, III has been stored for more than 3 weeks with only moderate decomposition as evidenced by only slight changes in its infrared spectrum. At higher temperatures (120–140°) with the concentrations chosen here, the decomposition is essentially complete in less than 30 minutes.

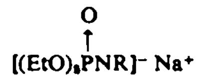
One limitation of this particular type of analysis is that the reaction appears to follow simple first order kinetics, where the conventional analysis indicates that there are two consecutive reactions involved in the mechanism. This can be rationalized by recalling that DTA is a method for measuring heat effects during reactions. The heat of reaction for the second transformation ($IV \xrightarrow{k_b} V + N_2$) is suggested from the conventional analysis to be small compared to the heat of formation of the intermediate. This is not unreasonable especially since the pre-exponential factor for the second reaction is less than 10^{13} implying that ΔS^* is less than 0 for the transition state leading from IV to V. The close agreement between the rate constants obtained by DTA analysis (k_a' in Table 5) and that obtained by a conventional analysis (k_a in Table 1) indicates that this is likely. Another possibility could be that, since the DTA reflects only heat changes, the overall rate observed as first order is not grossly affected by the second reaction since it is very much faster than the first reaction. That is, the two reactions cannot be independently resolved by DTA.

Conventional analysis. From the kinetic results obtained, the decomposition of III is best explained as proceeding through an ionic intermediate IV. A similar reaction of II and dimethylisobutenylamine appeared to go through a dipolar ion in the decomposition of a suspected triazoline intermediate as was evidenced by a strong absorption band at 2100 cm^{-1} in the IR spectrum.[16] Only a band of low intensity was observable in the decomposition mixtures of III at low temperatures and was not consistently present. Attempted chromatography of a solution of III on alumina gave a complex mixture (including V) which did show an intense band at 2100 cm^{-1}. The lifetime of IV is undoubtedly short as indicated from the k_b values. Supporting evidence is afforded by the classic kinetic data which best fits a reaction mechanism involving two consecutive first order reactions. (See Results for the determination of the kinetics of this decomposition.) The dependence of the reaction rate constant (for decomposition of III) upon solvent polarity (Table 4) supports this postulate also. It is well known that reactions which show a kinetic dependence on the polarity of the solvent, often involve an ionic species in the mechanism.[7] In the present example that an ionic species is formed is suggested by the increase in the rate constants, k_a and k_b, with increase in dielectric constant of the solvent.

A dipolar ion intermediate has been proposed[17–19] to explain the formation of the observed products in the decomposition of triazolines to form aziridines, imines and diazo compounds. In the system under discussion it is noteworthy that the N-substituted phosphoramidate anion portion of the dipolar ion IV[20] resembles the nitrogen analogs of the Wittig reagents VI[20] which are relatively stable. This fact suggests that the dipolar ion once formed could be stabilized by resonance delocalization involving d and p orbitals on phosphorus and nitrogen, respectively. Thus, for formation of V and IV, a six-membered transition state VII may be involved. Simultaneous loss of nitrogen and hydride shift could occur as the incipient C=N bond is being generated. It should be recalled that P → O bonds in general are highly polarized having high bond moments which would enhance the stability of VII.[21] A mechanism of this type is consistent with all observations and is not unreasonable,

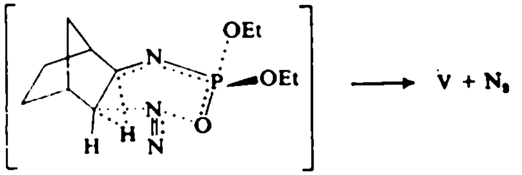


IV



$$[(EtO)_2\overset{O}{\overset{\uparrow}{P}}NR]^- Na^+$$

VI



VII

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[17] R. Fusco, G. Bianchetti, D. Pocar and R. Ugo. *Gazz. Chim. Ital.* **92**, 1040 (1962).

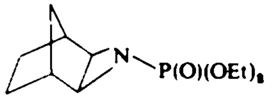
[18] For a review on this subject see R. Huisgen, *Angew. Chem.* (Int. Ed.) **2**, 565 (1963).

[19] C. H. Hassall and A. E. Lippmann, *J. Chem. Soc.* 1059 (1953).

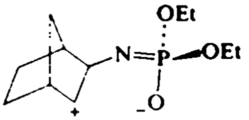
[20] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Org. Chem.* **29**, 2816 (1964).

[21] R. F. Hudson, *The Nature of the Chemical Bonding in Organo-phosphorus Compounds*, in *Pure and Applied Chemistry* Vol. 9; No. 2, p. 379 (1964).

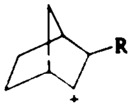
considering the large negative ΔS^* for the formation of products from the intermediate. It certainly explains why there is no evidence found for the aziridine VIII in the decomposition products of III. In analogy with the decomposition of the triazoline from benzoyl azide and norbornylene,[18] aziridine VIII would be expected if nitrogen were lost in a separate step. The resulting ion conceivably could be stabilized by electrostatic interactions such as illustrated in IX. If this were the case it is possible that ring closure (aziridine formation) could compete with hydride shift. An ion such as X would be a necessary postulate if nitrogen was lost in a separate step. It is well known that certain carbonium ions of general structure X undergo rearrangement,[22] and no rearranged products were found in the decomposition of III as evidenced by the good material balance. A carbonium ion such as XI has been proposed by Huisgen[18] as part of the mechanism in the formation of aziridine XII and oxazoline XIII from the decomposition of appropriate triazoline formed in the reaction of benzoyl azide with norbornylene. If the hydride shift occurs with simultaneous loss of N_2 in IV → V – N_2, it is unusual although the lack of rearrangement products expected from an



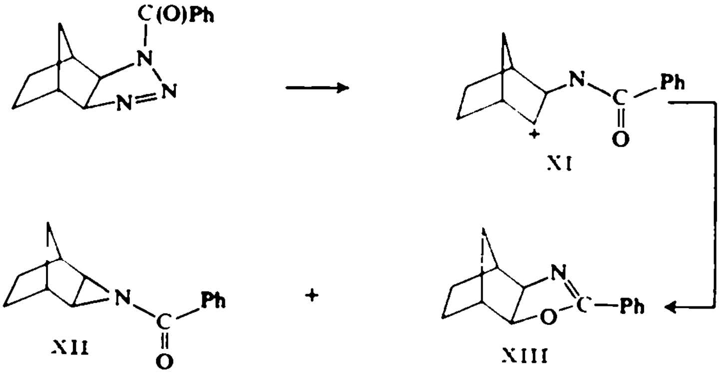
VIII



IX



X



XI

XII

XIII

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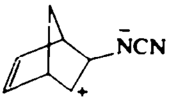
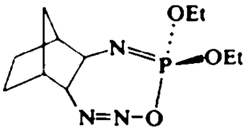
[22] J. A. Berson, *Carbonium Ion Rearrangements in Bridged Bicyclic Systems*, Chap. 3 in *Molecular Rearrangements* (Edited by P. deMayo) Part I. Interscience, New York, N.Y. (1963).

intermediate such as IX, does not allow an easy alternative explanation. In a recent case "hot ion" obtained from the decomposition of a suspected triazoline intermediate from reaction of norbornadiene and N_3CN, underwent molecular rearrangement.[23]



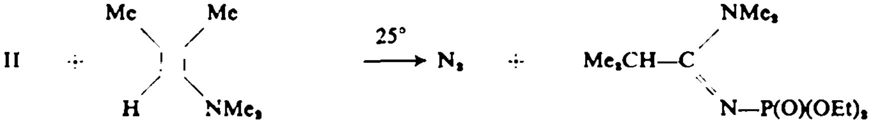
The E_a for Eq. 3 does seem higher than might be expected and it is tempting to speculate that an intermediate with phosphorus in a seven-membered ring may form in conversion of IV to V.[24] Under the conditions for decomposition of III to give V, such an intermediate could not be isolated nor detected. In any case, the lifetime of



such an intermediate must be short. The hydride shift required in obtaining V from IV certainly requires some energy of activation also.

Stabilization of the transition state VII may be enhanced by the *cis* arrangement of the vicinal groups in the dipolar ion and the restricted rotation of the C—N bonds imposed by the norbornylene system. As stated previously in the related example from this Laboratory, the rapid loss of nitrogen and subsequent formation of an amidine XIV was postulated in the reaction of II with N,N-dimethylisobutenlyamine.[1b]

Although a triazoline intermediate could not be isolated, intense absorption at



$$\text{II} + \begin{matrix}\text{Me} & & \text{Me}\\ & \text{C}=\text{C} & \\ \text{H} & & \text{NMe}_2\end{matrix} \xrightarrow{25^\circ} N_2 + \text{Me}_2\text{CH—C}\begin{matrix}\text{NMe}_2\\ \\ \text{N—P(O)(OEt)}_2\end{matrix}$$

XIV

2100 cm^{-1} in the IR spectrum of the reaction mixture suggests a dipolar[25] ion intermediate.[26] Consequently, stabilization of such a diazonium system by the phosphoryl function could logically arise through ground state electrostatic interactions.

Acknowledgment –It is with pleasure that we gratefully acknowledge support by the Public Health Service, Grant Number CA 07202-03. We also express our sincere thanks to Mrs. Ruth Erbar and Dr. Robert Gebelt for invaluable discussions concerning the program formulation for the computer. We also express thanks to the Research Foundation, Oklahoma State University, for partial support.

[23] A. G. Anastassioun, *J. Org. Chem.* **31**, 113 (1966).

[24] Seven-membered rings including C, P, N, and O are well known, see R. S. Edmundson, *Chem. Ind.* 1770 (1962).

[25] IR absorption for the diazo group in a number of aliphatic diazo compounds has been reported to occur from 2014 to 2100 cm^{-1}; see P. Tates, B. C. Shapiro, N. Yoda, and J. Fugger, *J. Amer. Chem. Soc.* **79**, 5757 (1957).

[26] It was recently reported from this Laboratory that the triazoline obtained from norbornylene and methyl azidoformate is unstable and decomposes rapidly, see A. C. Oehlschlager, P. Tillman and L. H. Zalkow, *Chem. Commun.* 596 (1965). Triazolines with electron-withdrawing groups attached to nitrogen in the ring are rare but a recent summary is available; see P. Scheiner, *J. Org. Chem.* **30**, 7 (1965). Possible triazoline intermediates in reactions of phosphorus azides with vinyl ethers have been reviewed; see K. D. Berlin and M. A. R. Khayat, *Tetrahedron* **22**, 975, 987 (1966).