

STUDIES OF RDX AND RELATED COMPOUNDS

XI. THE CONVERSION OF PHX TO AcAn¹

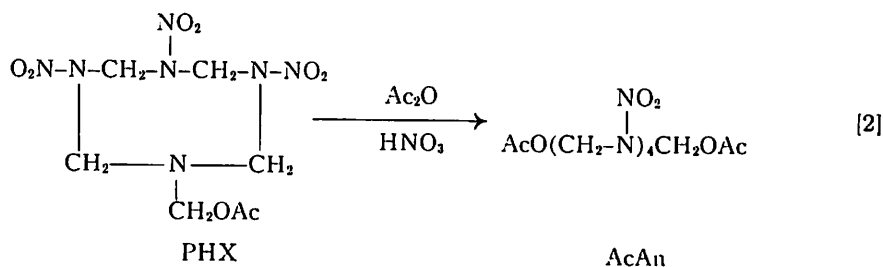
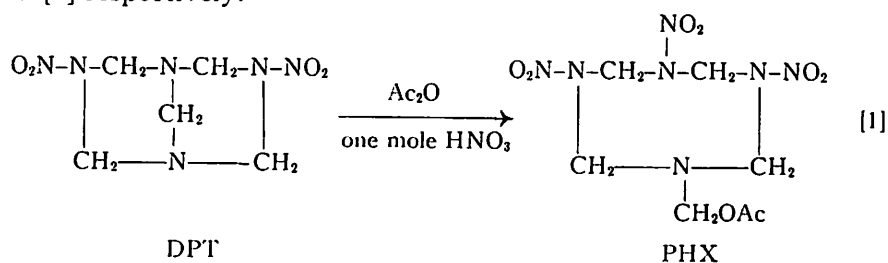
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ABSTRACT

The formation of AcAn from PHX, nitric acid, and acetic anhydride has been investigated at various temperatures. The effects of added acetic acid and added salts have been determined. While the reaction is first order with respect to PHX, it is of an order 2.6 with respect to nitric acid. The reaction rate is significantly decreased by small concentrations of sodium nitrate. The reaction is also characterized by a secondary salt effect and a low apparent activation energy of about 2 kcal. mole⁻¹. A mechanism has been suggested in qualitative, and to some extent quantitative, agreement with the experimental data. It is postulated that the conversion of PHX involves a rate-controlling ionic reaction between PHX and nitric acid, and that this is followed by a rapid acetylation of the acidic intermediate to AcAn.

INTRODUCTION

In the present paper of this series an attempt has been made to study in some detail a reaction of frequent occurrence in the chemistry of RDX and related compounds, namely the rupture of a methylene carbon-nitrogen bond. A search of the literature for a simple example of such a reaction, that is, where only one bond in the organic molecule was broken, revealed only two cases: (1) the formation of 2-acetoxymethyl-4,6,8-trinitrocyclotetramethylene tetramine (PHX) from 1,5-*endomethylene*-3,7-dinitrocyclo-2,4,6,8-tetramethylene-1,3,5,7-tetramine (DPT) and (2) the formation of 1,9-diacetoxypentamethylene-2,4,6,8-tetranitramine (AcAn) from PHX. These reactions are given in equations [1] and [2] respectively.



Although the former is too rapid for kinetic investigation the latter presents

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no such objection, and its study constitutes the bulk of the present work.

EXPERIMENTAL AND RESULTS

Materials

Nitric acid of approximately 99% concentration was prepared by vacuum distillation of a solution of 480 gm. ammonium nitrate in 600 ml. concentrated sulphuric acid at a pressure of 1 mm. and temperature 40°-65°C. The acid so obtained was either colorless or very pale yellow. Any nitrogen dioxide present was removed by bubbling dried air through the liquid. The acid was stored in the dark at 0°C. The acetic anhydride, approximately 95% pure (5% acetic acid), was obtained from Mallinckrodt (A.R.) or Merck (C.P.). It was used directly without further purification and no appreciable difference was observed with the use of either sample.

The PHX was prepared from DPT which, in turn, was made from hexamine according to Bachmann's procedure (1). Solutions of 1.5 moles hexamine in 5.5 moles of acetic acid and of 3 moles of 99% nitric acid in 3.5 moles acetic anhydride were added continuously and in equivalent amounts to one mole acetic acid over a 60 min. period, at 27° to 30°C. The solution was cooled and stirred vigorously while the addition was made, and the stirring was continued for 30 min. after it was completed. Dilution with 800 ml. water at 65°C. yielded a precipitate of DPT which was filtered off, washed thoroughly with water, and recrystallized from acetone. To 5 gm. of DPT suspended in 23 ml. acetic anhydride was added 1 ml. of 99% nitric acid. PHX precipitated before all the DPT went into solution. The precipitate was filtered immediately and washed with a few milliliters of acetone. It melted at 152-3°C.

Although PHX has never been recrystallized from any solvent, different batches of PHX gave exactly similar AcAn yield-time data. The PHX obtained was therefore considered to be sufficiently pure for use in the present investigation. An impurity was isolated, however, and found to be present to the extent of 4% by weight. The results were indirectly corrected for the presence of this contaminant in a manner described later.

Experimental Procedure

Solutions of "acetyl nitrate" were prepared (a) by pipetting the appropriate volume of nitric acid (at 0°C.) into an exact volume of acetic anhydride in a flask, (previously cooled in an ice bath) for each sample, or alternatively (b) by preparation of a fresh stock solution of nitric acid in acetic anhydride and withdrawal of aliquots for each experiment. Because of the large quantities of heat evolved, the acetic anhydride was, in the latter case, cooled to -78°C. before, and during, the addition of nitric acid. Aliquots were diluted with water to a standard volume and titrated for nitric acid with standard base, to a given pH as determined by a blank, according to the method of Betts, Stuart, and Winkler (3). Again the solutions, if not colorless, were rendered so by the same procedure as for nitric acid, described earlier. With the precaution of storing them in the dark at 0°C. they did not change titer over a period of at least eight hours. The presence of nitrogen dioxide had to be avoided since it was found to lower the yield of AcAn significantly.

Stoppered flasks containing the acetyl nitrate were placed in a thermostat, equipped with a mechanical shaker, and controlled to $\pm 0.1^\circ\text{C}$. After an interval of 10 min., during which the solution attained thermal equilibrium, the PHX was added. The solid dissolved almost completely in 30 sec. After appropriate reaction times the samples were diluted with distilled water to a standard volume, the mixtures allowed to stand for three days to ensure complete precipitation of AcAn, and then filtered through tared sintered glass crucibles and dried at 110°C . for several days. The data have been corrected for solubility losses which amounted to 10% of the weight of product on the average.

Variation of PHX concentration was limited by its small solubility in the reaction medium (e.g. at 35°C . the solubility in 20 ml. of solution was 0.5 gm. while at 15°C . it was 0.15 gm.).

In the experiments with added salts a weighed amount of salt was dissolved in 99% nitric acid and the solution diluted with the acid to a standard volume at 0°C . Aliquots of this solution were then pipetted into given volumes of acetic anhydride. This procedure avoided the difficulties associated with the very small rate of solution of these salts in acetic anhydride-nitric acid media.

The effect of added acetic acid on the reaction rate was also investigated. Standard solutions of glacial acetic acid in 95% acetic anhydride were prepared and aliquots withdrawn for each sample. Variation of the acetic acid concentration was limited by the small solubility of PHX in the solutions.

Calculation of Rate Constants

The curves obtained with acid concentrations greater than one molar, while first order for a large part of the reaction, are characterized by a slow secondary reaction to give AcAn or other water insoluble material. Fortunately, this slow secondary reaction can be readily differentiated from the main reaction to give AcAn, and the true final yield of AcAn was obtained by an obvious extrapolation, as in Fig. 1. The yields of AcAn are in general not 100%, because of a side

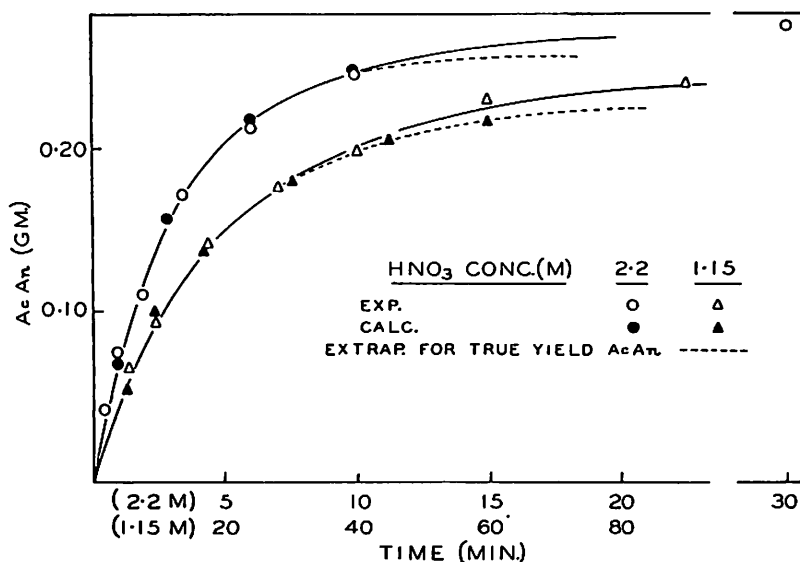


FIG. 1. Rate of AcAn formation at 15.1°C . with 0.0155 M PHX (0.20 gm.).

reaction. These competitive reactions were determined to be of the same order with respect to PHX.

It can readily be shown that the kinetic equations obeyed by two competitive first order reactions are given by

$$(k_m + k_s)t = 2.3 \log_{10} m/(m - x_m) \quad [3]$$

$$k_m/(k_m + k_s) = m/a \quad [4]$$

where a denotes the initial weight of PHX, m the true final yield of AcAn, while x_m and x_s represent the yields of AcAn and by-product obtained in time t , and k_m and k_s are the corresponding rate constants.

The constant $k_m + k_s$ was determined by substituting in equation [3] the value of m , a value of x_m and the corresponding value of t . As an added precaution, the AcAn yield-time curve was calculated from equation [3] with this value of $k_m + k_s$. Unless there was close agreement between calculated and experimental data, a small adjustment in m was made and the procedure repeated.

At low values of t the calculated results are in general slightly lower than the experimental data, because of the presence of the impurity mentioned earlier; the decomposition of this contaminant to give water-soluble products is complete at small reaction times. Consequently, for calculation of rate constants, the value of t chosen for insertion in equation [3] was about $t_{1/2}$. In addition, if the amount of impurity be taken into account, there is good agree-

TABLE I
EFFECT OF NITRIC ACID CONCENTRATION ON k_m

HNO ₃ conc.	10 ² k_m (min. ⁻¹) at PHX concentrations of:					
	0.0155 <i>M</i> at 15.1°C.		0.0232 <i>M</i> at 25.1°C.		0.0387 <i>M</i> at 25.1°C.	
2.2 <i>M</i>	31		39, 36		31, 32	
2.00	22				25	
1.60	12				13	
1.15	4.7				7	
1.00	3.8					
0.60	1.0		1		1	
	0.0155 <i>M</i>	0.0232 <i>M</i>	0.0310 <i>M</i>	0.0387 <i>M</i>	0.0516 <i>M</i>	0.0619 <i>M</i>
	at 35.1°C.					
		36	31, 32	31		31 18
					15(2)	
	6.1	6.1 9.2 1	6.0, 5.9 5.7, 9.2	5.4 0.8		4.8
0.93	0.0179 <i>M</i>	0.0238 <i>M</i>	0.0298 <i>M</i>	0.0476 <i>M</i>		
	5.1	5.1	4.6	3.7		

ment, even at small values of t , between the experimental and calculated curves. There is also fairly good agreement between the relative k_m 's and the corresponding initial rates. The constants k_m so obtained are accurate to better than ten per cent. The constants k_s , which are not determined as directly, are good only to about thirty per cent, and for this reason have not been given.

While the rate curves obtained with nitric acid concentrations greater than one molar were first order, this is not true for the lower acid concentrations. In the latter case the curves are characterized by a relatively rapid initial formation of AcAn followed by a slow secondary reaction. Because of this behavior, rate constants here were calculated by comparison of initial rates with data for 1.15 M acid, using the relative yield of AcAn in four minutes as a good approximation of the initial rates with these low acid concentrations. In this procedure the data were first corrected for the presence of the water insoluble PHX impurity, using results obtained on its rate of decomposition to water-soluble product, in the reaction medium.

Rate of Formation of AcAn

The experimental data on the effect of nitric acid, of added salts and of added acetic acid are summarized in Tables I, II, and III, respectively.

TABLE II
EFFECT OF ADDED SALTS ON k_m AT 35.1°C.

HNO ₃ conc. PHX conc.	2.2 M 0.0282 M		1.15 M 0.0295 M		1.15 M 0.0295 M	
	NaNO ₃ , M	$10^2 k_m$ (min. ⁻¹)	NaNO ₃ , M	$10^2 k_m$ (min. ⁻¹)	KClO ₄ , M	$10^2 k_m$ (min. ⁻¹)
	0	3.2	0	6.0	0	6.0
	0.000145	3.2	0.000076	5.3	0.00034	6.5
	0.00113	1.9	0.000101	5.2	0.00177	8.7
	0.00255	1.4	0.00059	2.9	0.00455	13.5
	0.00524	1.1	0.00119	2.1	0.00966	16.8
	0.0102	0.83	0.00534	1.0		
	0.0181	0.83	0.00960	1.0		

TABLE III
EFFECT OF ADDED ACETIC ACID ON k_m

HNO ₃ conc. (M) Temperature PHX conc. (M)	2.2 25.1°C. 0.0352 0.0211		1.15 35.1°C. 0.0352 0.0221		0.93 35.1°C. 0.0179
Added HOAc conc. (Vol. %)					
0	0.31	0.39	0.092	0.092	0.052
4	0.32				
10	0.32				
26	0.31	0.39	0.098	0.11	0.072

From the data obtained at 15.1°C., a plot of $\log k_m$ vs. $\log (\text{HNO}_3)$ shows that the reaction order with respect to nitric acid is 2.6. The small temperature coefficient of AcAn formation corresponds to an apparent activation energy of 2 kcal. mole⁻¹. In contrast, the corresponding value for the side reaction is of the order of 15 kcal. mole⁻¹.

Disappearance of Nitric Acid and of PHX

Using an electrometric method (3) for the estimation of nitric acid in aqueous acetic acid, it was observed that nitric acid reacted quantitatively, mole for mole, with PHX (though not with AcAn) in such media. This behavior necessitated the use of an analytical method for nitric acid applicable in the undiluted reaction medium. A suitable method, depending on the limited solubility of inorganic salts in these media was evolved; the details are given in an earlier paper (13).

These two analytical procedures determine the amount of nitric acid present in the diluted and undiluted reaction media, respectively. Since their values differ by an amount equivalent to the PHX present, a combination of these two methods provides a method for the estimation of PHX. However, this assumes that the products of the side reaction do not react with nitric acid on dilution of the reaction mixture. Since the amounts of nitric acid estimated by both methods were the same when reaction was complete, in spite of the by-products present, the above assumption is probably valid.

TABLE IV

RATE OF DISAPPEARANCE OF NITRIC ACID AND PHX AND RATE OF AcAn FORMATION WITH 1.17 *M* NITRIC ACID AT 35.1°C.

Reagents: 23.4 millimoles pale yellow nitric acid
6.20 millimoles PHX
20.0 ml. acetic anhydride

Time, min.	- ΔPHX , mM.	- ΔHNO_3 , mM.	ΔAcAn , mM.	$\Delta\text{PHX}/\Delta\text{AcAn}$
0	0	0	0	
20	1.55	2.85	0.75	2.1
60	3.0	4.1	1.35	2.2
120	3.6	5.2	1.95	1.85
240	5.75	7.6	2.8	2.05
360	5.85, 5.5	8.05, 8.3	3.3	1.8, 1.7

Because there is a large experimental error in the application of this analysis by difference to reaction conditions of high molar ratios of nitric acid to PHX, the determinations were made using low ratios of approximately four to one. However, the extent of the slow secondary reaction increased with decreasing acid concentration, thus placing, for theoretical purposes, a lower limit on the initial acid concentration which could be used. This necessitated the use of amounts of PHX which exceeded the solubility limit of the latter in the medium. It is therefore emphasized that the data given in Table IV were obtained under heterogeneous reaction conditions; this, however, does not detract from the conclusion drawn.

Some measurements of the rate of disappearance of nitric acid in homo-

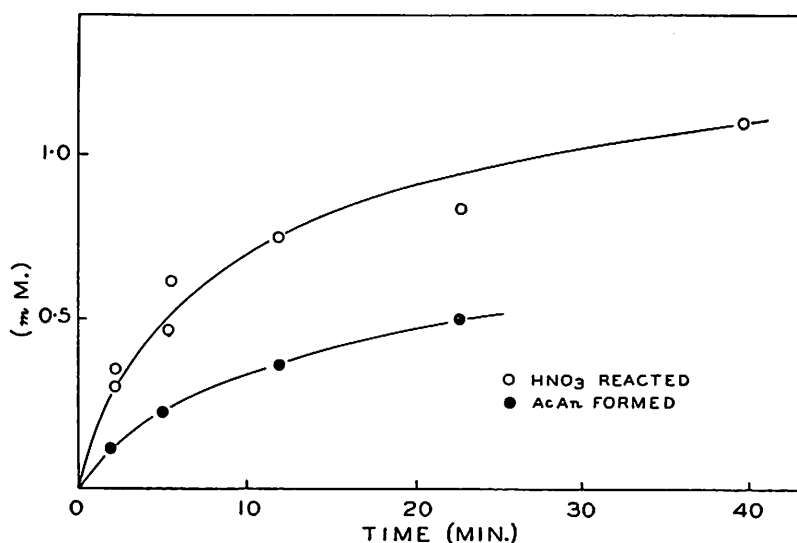


FIG. 2. Rate of AcAn formation and nitric acid disappearance with 1.15 *M* nitric acid and 0.0619 *M* PHX at 35.1°C.

geneous media were also made. Typical results are given in Fig. 2. The data show that the ratio of the rate of disappearance of nitric acid to the rate of formation of AcAn is approximately independent of the reaction time. The nitric acid reacted is greater than the AcAn formed although blank experiments without PHX showed no disappearance of nitric acid. Since the final yield of AcAn in these experiments was only about 50%, the difference is therefore due to a competitive reaction. Since the data obey Wegscheider's Test (20), this side reaction must be of the same order with respect to PHX as the main reaction, within experimental error.

A similar conclusion may be drawn from the data given in Table IV. However, in this case the acid concentration decreased from 1.2 *M* to 0.8 *M* during the course of reaction. Consequently, this conclusion is valid only if the ratio of rate constants for AcAn formation and side reaction is independent of acid concentration in this range. A direct measure of this ratio is the final yield of AcAn, as obtained by the extrapolation described earlier. Since this yield was found to be approximately constant over this range of acid concentration, the conclusion stands.

The data in Table IV also suggest that the nitric acid decomposition is greater than that of PHX. This fact may not be theoretically significant since in this case the acid was pale yellow and the excess consumed may have been due to autoreduction in the presence of nitrogen dioxide.

DISCUSSION

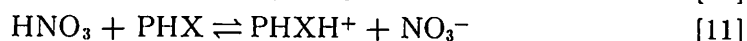
Summarizing the experimental data:

- The rate of formation of AcAn is proportional to $(\text{HNO}_3)^{2.6}(\text{PHX})$. However, the rate constant, k_m , falls off slightly with increasing PHX concentration.
- k_m is markedly decreased by added NaNO_3 but increased by KClO_4 .
- The reaction rate is markedly affected by concentrations of these added salts

therefore, that the ClO_4 group arising from KClO_4 exists largely as ClO_4^- rather than as unionized HClO_4 in $\text{HNO}_3\text{-Ac}_2\text{O}$ media.

Three possible effects of added salts are: repression of ionization by a common ion, primary and secondary salt effects. The second of these may be neglected in the first approximation since the activated complex of (6) is also a monovalent ion and therefore the ratio of activity coefficients in the theoretical expression for the rate constant is essentially independent of the ionic strength, μ .

It will be assumed that the concentration of the nitrate ion is appreciably greater than the more basic acetate ion in $\text{HNO}_3\text{-Ac}_2\text{O-AcOH}$ media so that $\mu = (\text{NO}_3^-)$ in the absence of KClO_4 . In addition to [5] the following equilibria probably occur in such media:



where S represents a solvent molecule and SH^+ , the conjugate acid. Another possible source of nitrate ions is the ionization of nitrogen pentoxide, which in turn might arise from the dehydration of nitric acid by acetic anhydride. However, *as a source of nitrate ion* these reactions are thermodynamically equivalent to reaction [5] if the nitracidium ion postulated there exists in the dehydrated form, NO_2^+ . The subsequent discussion of the salt effect is independent of the postulated form of nitracidium ion.

All ion activity coefficients, f , will be assumed to be given by the simple Debye-Hückel expression, $-\log f = A \sqrt{\mu}$, where A depends only on the absolute charge of the ion for a given medium. In this approximation, the activity coefficients of neutral molecules are essentially independent of μ . It also follows from datum (c) that the concentrations of PHX and of HNO_3 may be taken as essentially independent of added salt.

According to these assumptions there is no primary salt effect so that k_m is directly proportional to $(\text{NO}_2\text{OH}_2^+)$, while the latter is given by the equilibrium expression,

$$f^2(\text{NO}_2\text{OH}_2^+) (\text{NO}_3^-) = \text{const.} \quad [12]$$

From these relations and the previous expression for $\log f$ it follows immediately that

$$\log_{10} k_m (\text{NO}_3^-) = 2A \sqrt{\mu} + \text{const.} \quad [13]$$

Furthermore, addition of the expressions for the equilibrium constants of [5], [10], and [11] leads to

$$f^2(\text{NO}_2\text{OH}_2^+ + \text{SH}^+ + \text{PHXH}^+) (\text{NO}_3^-) = \text{const.} \quad [14]$$

In the absence of added nitrate the sum of the concentrations of these cations equals (NO_3^-) . From [13] and [14] it may then be concluded that

$$\log_{10} k_m = A \sqrt{\mu} + \text{const.} \quad [15]$$

To compare [13] and [15] with the data, an estimate of μ is necessary. The value of μ in the absence of added salt may be determined as follows. Denoting the concentrations of nitrate ion and of added sodium nitrate by y and x respectively, equation [14] may be written as

$$f^2(y - x)y = \text{const.} \quad [14']$$

Also, from equation [12] and the proportionality between k_m and $(\text{NO}_2\text{OH}_2^+)$,

$$k_m y f^2 = \text{const.} \quad [16]$$

Differentiating [14'] and [16] with respect to x , eliminating dy/dx between these equations, taking the limit of the resultant equation at $x = 0$ and neglecting a very small term involving df/dx (which is justified at $x = 0$)

$$\left[\frac{dk_m}{dx} + \frac{k_m}{y} \right]_{x=0} = 0. \quad [17]$$

Using this equation, the concentration of nitrate ion, y , at $x = 0$ was estimated from the limiting slope of a plot k_m vs. x (cf. Table II) to be $2.6 \times 10^{-4} M$ and ca. $8 \times 10^{-4} M$ when the nitric acid concentration was $1.15 M$ and $2.2 M$, respectively, the PHX concentration $0.0295 M$, and the temperature, 35.1°C .

In the presence of added nitrate, $\mu = y = (y - x) + x$. Elimination of yf^2 between [14'] and [16] leads to

$$(y - x) = \text{const. } k_m. \quad [18]$$

The proportionality constant may be determined from the previously estimated value of y at $x = 0$ and the corresponding value of k_m . The more accurate data at $1.15 M$ nitric acid were used for this purpose. The magnitude of $(y - x)$ may then be estimated from [18] for any value of x for which k_m has been determined. Since x is also known, μ may then be calculated.

With μ so estimated, equation [13] can be compared with the data on effect of added nitrate. In this equation $(\text{NO}_3^-) = \mu$. Using the data given in Table II, $(1.15 M \text{ HNO}_3, \text{ added NaNO}_3)$, $\log_{10} k_m(\text{NO}_3^-)$ was plotted vs. $\sqrt{\mu}$ in Fig. 3 and from the slope, $A = 5$.

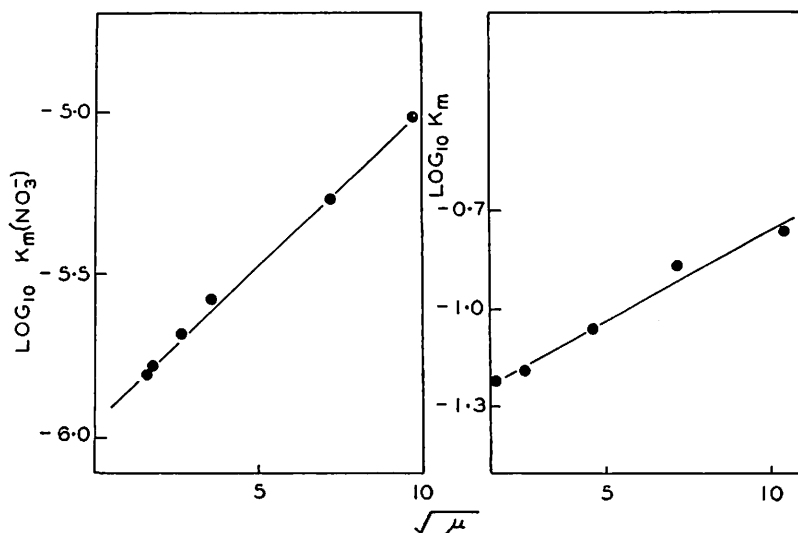


FIG. 3. Effect of ionic strength on rate of formation of AcAn.

In the presence of KClO_4 of concentration z , $\mu = (y + z)$ and y is given by [18] where x is now equal to zero. With μ thus determined, equation [15] was compared with the data on the effect of added KClO_4 given in Table II. The plot of $\log_{10} k_m$ vs. $\sqrt{\mu}$, given in Fig. 3, has slope, $A = 5$.

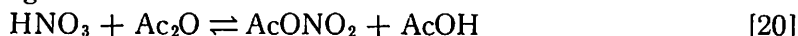
These experimental values of A may be compared with the theoretical value given by

$$A = \frac{z^2 e^3 \sqrt{2\pi N/1000}}{2.3(DkT)^{3/2}}$$

where N is Avogadro's number, D the dielectric constant of the medium, and the remaining symbols have their usual significance. At 35°C. the theoretical value of A is approximately equal to 4, assuming $D \cong 20$, the value for pure anhydride. The dielectric constant of acetic anhydride-nitric acid media has not yet been determined.

Order of Reaction with Respect to Nitric Acid

In the following, it will be assumed that nitric acid exists largely in the form of acetyl nitrate because of equilibrium (20), and that the nitrate ion arises mainly from [10] and [11] rather than from [5] owing to the presumed relative basicities and assumed low concentration of nitric acid. With these assumptions it is possible to derive an expression for the dependence of k_m on the acid concentration in good agreement with the data.



According to the second assumption the constant in equation [14] is directly proportional to (HNO_3) so that [14] becomes

$$f^2(\text{NO}_3^-)^2 = \text{const.} (\text{HNO}_3). \quad [21]$$

On the other hand the constant in equation [12] is proportional to $(\text{HNO}_3)^2$, while $(\text{NO}_2\text{OH}_2^+)$ is proportional to k_m , so that elimination of (NO_3^-) between [12] and [21] leads to

$$k_{\text{corr.}} = \text{const.} (\text{HNO}_3)^{3/2} \quad [22]$$

where $k_{\text{corr.}} = f k_m$.

$k_{\text{corr.}}$ is therefore given by [23] where $A = 5$

$$\log_{10} k_{\text{corr.}} = \log_{10} k_m - A \sqrt{\mu}. \quad [23]$$

If b denotes the stoichiometric concentration of HNO_3 and c the concentration of acetic acid originally present in the 95% acetic anhydride ($c = 0.8 M$), then $(\text{AcONO}_2) \cong b$ and $(\text{AcOH}) \cong (b + c)$, according to the first assumption. Elimination of (HNO_3) between [22] and the expression for the equilibrium constant of [20] then leads to

$$\text{const. } k_{\text{corr.}}^{2/3} = bc + b^2. \quad [24]$$

Finally, since $\mu = (\text{NO}_3^-)$, it follows from [21] and the expression for the equilibrium constant of [20] that, to a good approximation,

$$\mu = \text{const.} \sqrt{bc + b^2}. \quad [25]$$

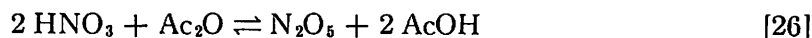
The proportionality constant in equation [25] was estimated from the data $\mu = 2.6 \times 10^{-4} M$ when $b = 1.15 M$ and $c = 0.8 M$. With μ thus determined for any value of b , $k_{\text{corr.}}$ was calculated from [23] and is given in Table V.

The proportionality constant in [24] was estimated from the value of $k_{\text{corr.}}$ at $b = 1.6 M$, namely, $k_{\text{corr.}} = 0.097 \text{ min.}^{-1}$. Equation [24] and the data are compared in Table V.

TABLE V
 COMPARISON OF EXPERIMENTAL AND THEORETICAL "*k*'s"

HNO ₃ , <i>M</i> "b"	<i>k_m</i> (min. ⁻¹)	<i>k_{corr.}</i> (min. ⁻¹)	
	Expt.	Expt.	Calc.
2.2	0.31	0.24	0.22
2.0	0.22	0.17	0.17
1.6	0.12	0.097	0.097
1.15	0.047	0.039	0.043
1.00	0.038	0.032	0.031
0.60	0.01	0.009	0.01

Considering the good agreement between the experimental and calculated values of $k_{\text{corr.}}$, a closer examination of the two assumptions made at the beginning of this section appears desirable. The very large heat of mixing of HNO₃-Ac₂O mixtures is quite noteworthy. This heat of reaction is almost certainly not to be attributed to ionization, which was seen in an earlier section to occur to a very minor extent. Furthermore, its magnitude is appreciably greater than would be expected from the changes in van der Waals or hydrogen bonding forces on mixing. Consequently, it appears that some chemical reaction such as the formation of acetyl nitrate or of nitrogen pentoxide via [20] or [26], respectively, occurs to an appreciable extent.



Some evidence concerning these equilibria has become available since the completion of the present work. An analysis (18) of the vapor of HNO₃-Ac₂O mixtures suggests that at 50% nitric acid the solution is mainly acetyl nitrate, while nitrogen pentoxide is an important constituent at higher acid concentrations and acetyl nitrate at lower ones.

From a comparison (9) of the near ultraviolet absorption spectra of these mixtures with that of nitrogen pentoxide solutions, Jones and Thorn inferred that nitric acid existed largely as nitrogen pentoxide in these media, both at high and low stoichiometric concentrations of nitric acid. However, no comparison with acetyl nitrate solutions was given and a more detailed study of the spectra is necessary. From an examination of the structures of nitrogen pentoxide and of acetyl nitrate, and of the spectra (9) of nitrogen pentoxide and of ethyl nitrate, it seems possible that these results may also be consistent with the presence of large concentrations of acetyl nitrate in these media. While it has been suggested that acetyl nitrate is either not present in this medium or is formed very slowly (5, 11), the published data are not inconsistent with the assumptions of the present paper.

It is also of interest to observe that acetyl nitrate can be prepared by a vacuum distillation of mixtures of nitrogen pentoxide with acetic anhydride (4, 16). Finally, postulation of equilibrium [26] rather than of [20] does not appear to lead to quantitative agreement with the observed effect of nitric acid on k_m .

However, it seems clear that the composition of nitric acid – acetic anhydride media is not yet definitely established.

The effect of added acetic acid is qualitatively consistent with the present assumptions but is smaller than would be expected from equation [24]. This equation neglects the extent of dimerization of acetic acid (12) and the possible greater basicity of acetic acid as compared with acetic anhydride, both of which become increasingly important effects at higher concentration of acetic acid. The latter effect would increase the nitrate ion concentration and thereby tend to repress the formation of nitracidium ion. It can be shown that both effects provide a qualitative explanation of the discrepancy between the calculated and observed effects of added acetic acid.

The slight decrease of k_m with increased PHX concentration can be attributed to the corresponding increase of nitrate ion and the resultant decrease of nitracidium ion concentration by the common ion effect.

According to the mechanism presented, the apparent activation energy of 2 kcal. per mole represents the activation energy of the rate determining step (reaction 6) together with the temperature coefficient of the concentration of nitracidium ion.

Finally, it is of interest to observe that the nitration of PHX in nitric acid – acetic anhydride media is rather similar to the nitration of benzene in the same media. It was found (5) that the latter reaction was first-order with respect to benzene, approximately third-order with respect to nitric acid, and was accelerated by added acetic acid. However, its apparent activation energy, 12 kcal. mole⁻¹, is appreciably higher than that found for the nitration of PHX. The analogous behavior of the nitration of PHX and benzene in this solvent and the interpretation of the nitration of substituted benzenes in the same solvent by a nitracidium ion mechanism are consistent with the mechanism outlined in the present paper.

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