15% as large (the ionic strength being kept constant with 0.0690 *N* sodium perchlorate)

$$k[\mathrm{OH^-}]' + k'[\mathrm{CH_3NH_2}]' = (6.48 \pm 0.08) \times 10^{-4} \quad (6)$$

From the known strengths of the methylamine buffer solutions used and the value of *k* from Table II, No. 3 (no. 1 and 4 show that the ionic strength effect is not large), equations 5 and 6 can be solved simultaneously with two ionization constant expressions for methylamine to yield the results

$$[\mathrm{OH^-}] = 9.7 \times 10^{-4} \qquad [\mathrm{OH^-}]' = 8.7 \times 10^{-4}$$
$$k' = 3 \times 10^{-4} \qquad K_i^{\mathrm{CH_3NH_2}} = 7.27 \times 10^{-4}$$

The value for the ionization constant of methylamine is in surprisingly good agreement with a value 7.24 × 10^{-4} interpolated from the data of Everett and Wynne-Jones.[12] While we believe that we have demonstrated general base catalysis for the reaction, the value of *k'*, having been obtained from a small difference between two large numbers, may be considerably in error.

In relation to the kinetic isotope effect, the rate of exchange of chloroform in alkaline 99.8% deuterium oxide solution was studied. Although reversibility is greater in this case, it is still minor compared to the experimental error and a kinetic equation analogous to 3 was used to calculate the rate constant shown in Table II, No. 6. Although this rate constant is more than twice that for deuterochloroform in protium oxide solution, part of the increased reactivity may be due to the generally increased reactivity of the deuteroxide ion in deuterium oxide solution over the hydroxide ion in aqueous solution.[13]

[12] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941).

[13] S. H. Maron and V. K. La Mer [THIS JOURNAL, **60**, 2588 (1938)] point out increases of 39–42, 36, 33, 22 and 20% for five different reactions.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Mechanism of the Homogeneous Alkaline Decomposition of Cyclotrimethylenetrinitramine: Kinetics of Consecutive Second- and First-order Reactions. A Polarographic Analysis for Cyclotrimethylenetrinitramine[1]

BY WALTER H. JONES

RECEIVED APRIL 27, 1953

The mechanism and kinetics of the reaction of methoxide ion with cyclotrimethylenetrinitramine in absolute methanol have been studied, both with and without added neutral salt, in the temperature range 19.00–44.93°. The stoichiometry and kinetics were interpreted in terms of the mechanism given in steps 1–4 where the base C^- is of intermediate strength, titratable at neutral but not at alkaline *p*H. From knowledge of k_1 and the total rate of production of nitrite, it was possible by mathematical analysis to evaluate k_2. The experimental rate of production of nitrite could then be fitted satisfactorily by means of k_1 and k_2 for at least 85% of the reaction. Added neutral salt depressed k_1 slightly, but had a larger positive effect on k_2. Enthalpies and entropies of activation are reported, and the results interpreted in terms of possible structures for the intermediates. A polarographic analysis for cyclotrimethylenetrinitramine has been developed, valid to ±2.5%. This compound gave at least three polarographic waves in absolute methanol at *p*H 7.4 (borate buffer) and 30.1°. The first, $E_{1/2} = -0.811 \pm 0.001$ v. (*vs.* S.C.E.) was used for analytical purposes; the concentration was, in the range employed, linear with diffusion current.

Somlo[2] has identified a number of products of the heterogeneous decomposition by hot concentrated aqueous alkali of the high explosive cyclotrimethylenetrinitramine (hereinafter called RDX). While the present study was in progress, Epstein and Winkler[3] reported briefly on the homogeneous decomposition in aqueous acetone but did not determine products or undertake a detailed kinetic study. The present paper describes an investigation of the stoichiometry and kinetics of the homogeneous reaction in methanol solution.

Since the initial reaction of secondary nitramines with alkali has been reported to be the elimination of nitrous acid,[4–6] we have studied the production of nitrite ion, destruction of RDX, and disappearance of alkali during the course of the reaction. Methanolic solutions of potassium hydroxide and both sodium and lithium methoxides were employed as bases; for purposes of illustration, methoxide ion will be used in subsequent formulations.

All of the kinetic and stoichiometric results could be rationalized in terms of the mechanism

$$\mathrm{RDX} + (\mathrm{OCH_3^-}) \xrightarrow{k_1} \mathrm{A} + \mathrm{CH_3OH} + (\mathrm{NO_2^-}) \quad (1)$$

$$\mathrm{A} + (\mathrm{OCH_3^-}) \xrightarrow{\text{fast}} (\mathrm{B^-}) + \mathrm{CH_3OH} \quad (2)$$

$$\mathrm{B^-} + (\mathrm{OCH_3^-}) \xrightarrow{\text{fast}} (\mathrm{C^=}) + \mathrm{CH_3OH} \quad (3)$$

$$(\mathrm{C^=}) \xrightarrow{k_2} \mathrm{D^-} + (\mathrm{NO_2^-}) \quad (4)$$

Here $C^=$ is a base of intermediate strength, quantitatively titratable at neutral (brom thymol blue) but not at alkaline (phenolphthalein) *p*H. B^- and D^- are weaker bases which build up late in the reaction at the expense of (OCH_3^-) and lead to a

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[1] Material supplementary to this article has been deposited as Document number 4104 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[2] F. Somlo, *Z. ges. Schiess-u. Sprengstoffw.*, **35**, 175 (1940); *C. A.*, **35**, 319^1 (1941).

[3] S. Epstein and C. A. Winkler, *Can. J. Chem.*, **29**, 731 (1951).

[4] A. P. N. Franchimont and H. van Erp, *Rec. trav. chim.*, **14**, 224 (1895).

[5] H. van Erp, *ibid.*, **14**, 48, 242, 327 (1895); **15**, 166 (1896); *Ber.*, **30**, 1251 (1897).

[6] A. H. Lamberton, *Quart. Rev.*, **5**, 75 (1951).

buffering action; at late stages of reaction, potentiometric titrations with strong acid gave *p*H curves typical of a mixture of a strong base with one or more weak bases. Suggested structures for the intermediates will be given below.

It was found that RDX underwent a slow solvolysis in pure methanol to produce nitrite. This resulted in a certain degree of complexity in interpreting the stoichiometry involved, since its relative importance was a function of the alkali concentration. The reaction was too slow, however, to affect the kinetics at the temperatures used for rate studies.

Kinetic Results

The following symbolism will be employed

a	initial molarity of (OCH_3^-)
b	initial molarity of RDX

At a time t

x	total nitrite molarity
x_1	molarity of nitrite from reacn. 1
x_2	molarity of nitrite from reacn. 4
R	RDX molarity
Z	(OCH_3^-) molarity (alkali normality found by phenolphthalein alkalimetry)
C	molarity of species ($C^=$)
Y	$= Z + C$ (alkali normality found by brom thymol blue acidimetry)

Values for k_1, defined as the specific rate of production of x_1, were derived by four independent analytical procedures: nitrite estimation, RDX determination, brom thymol blue acidimetry and phenolphthalein alkalimetry. By setting up the necessary stoichiometric relations and assuming stationary state concentrations of the unstable intermediates A and B^-, we may derive the equations

$$dx/dt = k_1(a - 3x_1)(b - x_1) + k_2(x_1 - x_2) \qquad (5)$$

$$-\,dR/dt = k_1(R)(a - 3b + 3R) \qquad (6)$$

$$-\,dZ/dt = k_1(Z)(3b - a + Z) \qquad (7)$$

$$-\,dY/dt = k_1/2\,(3Y - a)(Y + 2b - a)^7 \qquad (8)$$

Equations 5–8 were integrated (the second term of the right-hand member of 5 being dropped), the appropriate limits were substituted, and k_1 values were derived from the least squares slopes of plots of the resulting concentration functions against time. Graphical rather than analytical methods were used in order to avoid giving undue weight to the initial changes in concentration and time, which were subject to the greatest experimental error.

In Table I are summarized the results of determinations of k_1 at temperatures from 19.00 to 44.93° both with and without added neutral salt, which depressed the rate (*e.g.*, *cf.* data 1 and 3). In the ionic strength range 0.45–0.65 there was no detectable trend in rate constant, and such results were averaged and recorded as $\mu = 0.5$. The ionic strength was fixed with added sodium perchlorate except for two runs (datum 4) in which lithium chloride was used. The latter salt appeared to give a significantly greater reduction in rate: this phenomenon was not investigated further.[10] Potassium hydroxide rate constants were about 20% higher than the corresponding methoxide values (*cf.* data 13 and 5).

TABLE I

k_1 VALUES

No.	Temp., °C.	Method of analysis[a]	n[b]	μ[c]	k_1[d]
				NaOCH$_3$ as base	
1[e]	44.93	a	9	0.005–0.016	4.08 ± 0.07
2	44.93	b	2	.011	4.13 ± .18[f]
				.016	3.71 ± .10[f]
3	44.93	a	4	.5	2.65 ± .01
4	44.93[g]	a	2	.5	1.81, 1.99
5	30.14	a	5	.002–0.015	0.441 ± 0.003
6	30.12	c	1	.010	.466 ± .011[f]
7	30.14	a	9	.5	.285 ± .06
8	30.12	d	1	.11	.303
9	30.12	d	5	.5	.221 ± .007
10	20.56	a	7	.005–0.016	.1006 ± .0008
11	20.56	a	5	.5	.0635 ± .0013
12	19.00	a	3	.010–0.018	.0729 ± .0032
				KOH as base	
13	30.11	a	3	0.005–0.010	0.525 ± 0.003
14	30.06	d	4	.010	.481 ± .011

[a] Methods: a, (NO_2^-) determination; b, RDX analysis; c, phenolphthalein alkalimetry; d, brom thymol blue acidimetry. Two nitrite runs, which are not included in this summary, were rejected on a statistical basis.[8,9] [b] n = number of kinetic runs. [c] $\mu = a +$ neutral salt concentration. NaClO$_4$ added in numbers 3, 7, 8, 9 and 11. [d] Units, l. (mole min.)$^{-1}$. Except as noted, the ± values are standard errors of the means, *i.e.* $S/\sqrt{n}$, where S is the standard deviation. [e] Includes two runs with LiOCH$_3$ as base; these did not differ significantly from the others. [f] ± values are standard deviations of the least squares slopes.[8,9] [g] LiCl used as neutral salt.

If the mechanism formulated is valid, all four procedures should give similar values for k_1. Since the methods were not used under a single set of conditions, we shall compare the results of the other three with the initial rate of production of nitrite. The bulk of the data were from nitrite analysis, since this was the most accurate determination and since nitrite data were necessary for the estimation of k_2.

Necessarily, the nitrite data gave upper limit values for k_1, and the straight line plots held for varying extents of reaction, depending upon the value of a/b and the ionic strength. Since (see below) k_2 was subject to a moderate positive salt effect, the nitrite data obeyed the derived rate law best at low values of a/b and ionic strength (as far as 80–90% reaction in some cases). With a varia-

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(7) This equation is applicable only to the initial portion of the reaction. More nearly rigorously, $-\,dY/dt = 2k_1(R)(Z) + (dx_2/dt)$; neglect of x_2 gives equation 8.

(8) T. B. Crumpler and J. H. Yoe, "Chemical Computations and Errors," John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 186 ff.

(9) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, page 42.

(10) Possibly it is due to a reduction in the basicity of the solution because of the formation of LiOCH$_3$; LiOH, for example, behaves as though incompletely ionized in aqueous solutions: L. C. Darken and H. F. Meier, THIS JOURNAL, **64**, 621 (1942). Lithium salts were investigated in order to study salt effects on the RDX kinetics, since perchlorates interfered with this analysis; this project was not concluded.

tion of about sixfold in a/b[11], the results for k_1 by this method were identical within experimental error.

For the determinations of k_1 by RDX analysis, using equation 6, we may compare data 1 and 2. In principle, this analysis should have been the best procedure for evaluating the rate constant since, unlike the other procedures, it was not subject to complications due to subsequent reactions; these data, in fact, gave linear plots throughout the entire course of reaction. The RDX analysis used (see Experimental) was, however, the least precise of the four and was rather tedious; consequently, only a sufficient number of runs was made to demonstrate the validity of the rate law. The decrease in k_1 on increasing a (and therefore μ) seemed significant, and probably was attributable to the negative salt effect. Such an effect was not noticeable in the nitrite data, but in this case the salt effect may have been obscured by an increasingly positive error in k_1 resulting from the enhanced importance of x_2 as a/b was increased.

The use of equation 7, applicable to phenolphthalein alkalimetric determinations, is illustrated by comparison of data 5 and 6. Equation 7 held for datum 6 as far as the run was carried, in this case 70% of reaction.

The case of the determination of k_1 from equation 8 is exemplified by comparing data 13 and 14 of Table I. The upper limit value of 0.525 l. (mole min.)$^{-1}$ from nitrite analysis is to be compared with the 0.481 l. (mole min.)$^{-1}$ from acidimetry. Although equation 8 would be expected to give upper limit values for k_1,[7] experimentally it was found that the analysis gave increasingly positive errors in y as the reaction proceeded, because of the buffering action mentioned previously, and the plots of the integrated form of equation 8 (time as abscissa) invariably eventually became concave downward. Hence the acidimetric k_1 is probably a lower limit.

In estimating the precision of the k_1 determinations, the standard deviation of the least squares slope was used.[9] At worst, for the nitrite runs at 44.93° (datum 1, Table I), the average standard deviation for the set was 3.6% of k_1. This is probably an upper limit, since this set of nitrite data showed the greatest scatter from linearity; this scatter was probably due to the small number of points and short time intervals involved in the linear portions of the plots at this temperature and ionic strength. The standard errors of the mean of the nitrite sets (excluding datum 4) averaged 1.1% of k_1; this indicates the reproducibility of k_1 over the a/b range used.

Plots of log (k_1/T) against $(1/T)$[12] for the nitrite data gave good straight lines, and from the least squares slopes and intercepts the quantities of activation $\Delta H^{\ddagger} = 27.9 \pm 0.4$ kcal./mole and $\Delta S^{\ddagger} = 23.6 \pm 1.3$ e.u. were found for the runs with no added salt; at $\mu = 0.5$, $\Delta H^{\ddagger} = 27.9 \pm 0.4$ kcal./mole and $\Delta S^{\ddagger} = 22.7 \pm 1.2$ e.u. (the indicated errors were calculated from the standard deviations of the slopes and intercepts[9]).

It was of interest to test further the proposed rate law by determining whether the nitrite concentration might be expressed as a function of time in terms of k_1 and a second parameter, k_2. This is interesting kinetically, for the mechanism essentially consists in consecutive second- and first-order reactions producing the same product. To obtain x as a function of t, we must solve the equations

$$\mathrm{d}x_1/\mathrm{d}t = k_1(a - 3x_1)(b - x_1) \qquad (9)$$

$$\mathrm{d}x_2/\mathrm{d}t = k_2(x_1 - x_2) \qquad (10)$$

Solutions for x_2 as a function of t by a standard method[13] gave, on combination with the solutions of 9 for x_1[14]

If $a < 3b$

$$x = \frac{b[e^{k_1(3b-a)t} - 1]}{(3b/a)e^{k_1(3b-a)t} - 1} + Ce^{-k_2t} + a/3 + k_2\left(b - \frac{a}{3}\right)\sum_{n=1}^{\infty}\left[\frac{((a/3b)e^{-k_1(3b-a)t})^n}{nk_1(3b - a) - k_2}\right] \qquad (11)$$

If $a = 3b$

$$x = \frac{3k_1b^2t}{1 + 3k_1bt} + Ce^{-k_2t} + b$$

$$\frac{-k_2}{3k_1}\,e^{\frac{-k_2(1 + 3k_1bt)}{3k_1b}}\left\{\ln(1 + 3k_1bt) + \sum_{n=1}^{\infty}\left[\frac{[(k_2/3k_1b)e^{(1+3k_1bt)}]^n}{n.n!}\right]\right\} \qquad (12)$$

C, an arbitrary constant, was selected to conform to the experimental condition that $x = 0$ when $t = 0$. To estimate k_2, we note that $(x_1 - x_2)$ will pass through a maximum at a certain stage of the reaction; at this time, $\mathrm{d}(x_1 - x_2)/\mathrm{d}t = 0$, and k_2 is derivable from equations 9 and 10 and knowledge of k_1 and the values of x and x_1. A value of x_1 was obtainable either from the known value of k_1 or from determination of RDX concurrently with nitrite.

The quantity $(a - 3x_1)$ was frequently a very small difference at the maximum, however, and a somewhat better fit to the data could sometimes be obtained if the value of k_2 derived graphically were used as only a first approximation in fitting equations 11 or 12 to the experimental results. Thus if we rewrite equation 11, noting that the first term of the right-hand member is x_1 and defining the last term as X, we obtain equation 13, or an analogous equation from 12.

$$k_2t = \ln\left(\frac{C}{x - x_1 - a/3 - X}\right)^{\text{[15]}} \qquad (13)$$

Plots of the right-hand term of 13 against t were linear. The second approximation to k_2 found from the slope could then be substituted into 13 and by iteration a new k_2 found. Usually, however, the second k_2 was nearly the same as that

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(11) The range of values was rather severely restricted by the very limited solubility of RDX in methanol and the attendant analytical difficulties; the highest attainable b was about 0.006 M. Methanol afforded the greatest possible range of any solvent tried, except the aqueous acetone of Epstein and Winkler (ref. 3). The reaction of alkali with the latter solvent was, however, a complicating factor.

(12) According to the equation $k = (kT/h)e^{\Delta S^{\ddagger}/R}e^{\Delta H^{\ddagger}/RT}$; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(13) M. Morris and O. E. Brown, "Differential Equations," Prentice-Hall, Inc., New York, N. Y., 1942, p. 34.

(14) In obtaining equation 11 it was found necessary to integrate a power series, and this integration was only valid for $t \geqq 0$, $a < 3b$; hence the rate law could be tested only for this case. Details of this integration and other mathematical steps reported here are available through ADI (ref. 1).

(15) Both C and $(x - x_1 - a/3 - X)$ are negative quantities.

found by the graphical procedure and it changed very little on further approximations. C proved to be virtually independent of k_2, and late in the reaction X contributed very little to $(x - x_1 - a/3 - X)$.

To illustrate the procedure, an example will be given in some detail. Both nitrite and RDX data were obtained on a run at 44.93°. From application of equation 5 to the first few nitrite determinations, $k_1 = 3.93 \pm 0.29$ l. (mole min.)$^{-1}$; equation 6 and the RDX data gave $k_1 = 4.13 \pm 0.18$ l. (mole min.)$^{-1}$. A large scale plot of nitrite concentration as a function of time was prepared, a smooth curve drawn through the points, and x read off at intervals. From the k_1 from RDX data,[16] x_1 was calculated at these times, and hence $x_1 - x_2$ (*i.e.*, $2x_1 - x$). This led to a value of 7.665×10^{-4} min.$^{-1}$ for k_2. C was then evaluated from equation 11 on setting $x = 0$ at $t = 0$ and substituting the values for the two rate constants. The series term converged fairly rapidly; it was carried to fourteen terms, the last contributing less than 0.01% of the total. C was -0.003742 M. These values for k_2 and C were substituted into equation 13 and an excellently linear plot resulted; the least squares slope, k_2, was 8.08×10^{-4} min.$^{-1}$. The process was repeated, values of $C = -0.003746$ M and $k_2 = 8.08 \times 10^{-4}$ min.$^{-1}$ being found. The fit to the data was then observed by calculating x as a function of t from the two rate constants and equation 11. (In this case only six terms of the series were necessary.) The results are plotted in Fig. 1. Also given are x_1 and $(x_1 - x_2)$. The fit of the data to the rate law is probably as good as the experimental accuracy.

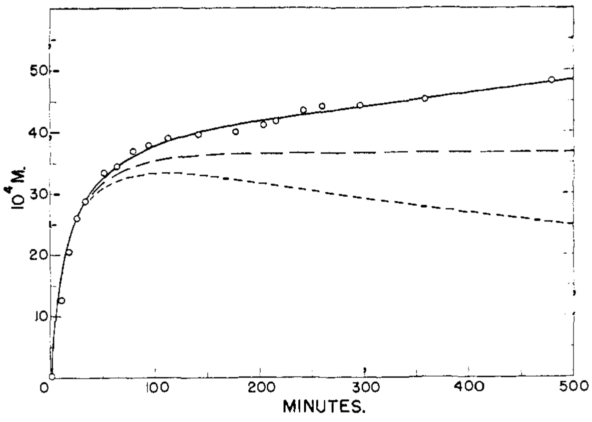

Fig. 1.—Nitrite concentration as a function of time: a, 0.011015 M; b, 0.005508 M, no added salt. Circles are experimental points; solid line is calculated from equation 13, using $k_1 = 4.13$ l. (mole min.)$^{-1}$ and $k_2 = 8.08 \times 10^{-4}$ min.$^{-1}$; dashed line is x_1 and dotted line is $(x_1 - x_2)$; M is molarity.

Although the fit was generally acceptable as far as it was feasible to carry a run, it was noted that for $a/b \leqq 1$ the fit was frequently good to no further than 85% reaction, whereafter the production of nitrite was too great to be accommodated by the rate law. Eventually, the production of nitrite might in these cases exceed the anticipated limit of $^2/_3\, a$.[14] Conceivably this was the result of the decomposition of D^- to give nitrite (see Discussion of Results), or of the reactions of RDX with solvent or with one or more of the intermediates B^-, $C^=$ or D^- to produce nitrite. The latter reactions would be expected to be of greatest importance at low a/b values.

The determination of k_2 involved measurement of $(2x_1 - x)$, which was particularly sensitive to errors in x and varied with the value used for k_1. Consequently, k_2 values were not particularly reproducible, as shown in Table II. The relative values of x_1 and x_2 during a run were functions of the temperature, ionic strength and initial reactant concentrations, and in only the few cases of Table II were the data carried far enough to show a maximum in the $(x_1 - x_2)$ curve and the large difference between x and x_1 necessary for a reliable estimation of k_2. At 20° the reaction was so slow that in no case was it followed sufficiently far to show a maximum value of $(x_1 - x_2)$.

TABLE II

K_2 VALUES[a]

No added salt			$\mu = 0.5$		
10^3a	10^3b	10^4k_2	10^3a	10^3b	10^3k_2
		44.93°			
10.96	5.48	7.5	6.22	6.21	7.9
11.02	5.51	8.1	11.65	5.82	7.6
11.37	5.68	12	15.95	5.32	4.2
	Mean	9.2 ± 1.4		Mean	6.6 ± 1.2
		30.14°			
5.33	5.33	7.76	5.47[b]	5.53	1.4
10.36	5.18	7.99	5.47[b]	5.53	1.0
15.13	5.04	7.58	9.01[b]	4.50	1.4
			9.01[b]	4.50	0.97
			13.20	4.40	1.01
	Mean	7.78 ± 0.12		Mean	1.16 ± 0.10

[a] Units min.$^{-1}$, a and b in moles/l. ± values are standard errors of the means (*cf.* Table I). [b] Duplicate runs, but by different operators. Three significant figures are reported when the fit to the data seemed particularly good.

Thes pread and paucity of values in Table II are obviously too great to make possible a significant determination of the activation quantities, but a $\Delta H^{\ddagger}$ lower than that for k_1 and a negative rather than positive $\Delta S^{\ddagger}$ are indicated (*e.g.*, the runs with added salt gave $\Delta H^{\ddagger} = 22$ kcal./mole and $\Delta S^{\ddagger} = -8$ e.u.). Also, k_2 is subject to a moderate positive neutral salt effect, in contradistinction to k_1. There is no distinct trend in the rate constants with changing initial alkali concentration.

Discussion of Results

Since we were unable to identify any of the organic intermediates indicated by the kinetic analysis, proposals regarding their structures will be wholly speculative. By opening the RDX ring it is not difficult to devise schemes for obtaining all of the reported products, but we were unable to reconcile any of these formulations with the observed stoichiometry and kinetics and prefer to regard the

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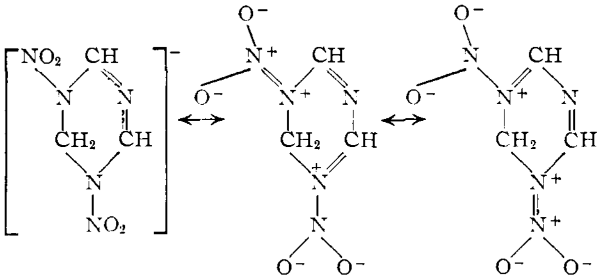
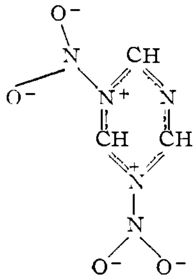
[16] A somewhat better fit to the nitrite data could be gotten by using the nitrite k_1, but it was desired to use the k_1 value derived by an independent procedure.

ring as intact under the relatively mild conditions of the kinetic experiments. Thus we may suggest that A is the product of HNO_2 elimination, *i.e.*, 1,3,5-triaza-3,5-dinitrocyclohexene-1. For B^- we may write the resonating system[17]



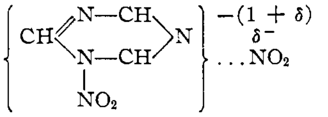
and for $C^=$ a structure with aromatic-type resonance



Similarly, D^- may be written as a resonance hybrid of five important structures.[18]

The most reasonable mechanism for the first step in the decomposition would seem to be concerted E2 elimination of nitrite by attack on an RDX methylene hydrogen, which may be rendered acidic by the adjacent nitramine groups.[17] This would be analogous to the structurally similar reaction of alkali with *p*-toluenesulfonbenzylmethylamide,[19] and would also represent a nitrogen analog of the carbonyl elimination reaction ($E_{CO}2$) of organic nitrates studied by Baker and Easty.[20] If this is the case, the large positive entropy of activation for k_1 might be explained by means of a "smearing" of the charge over the lengthy five-center transition state which may result in decreased solvent orientation relative to that around the methoxide ion.[21] The very small negative salt effect on k_1 might also be attributable to charge dispersal, since this might be inhibited by increases in ionic strength.[22] This salt effect appears to be largely in the entropy term, but the uncertainties in the quantities of activation allow no conclusions on this score.

Conclusions regarding k_2 will admittedly have little experimental basis. Nevertheless, we have noted a moderately small positive salt effect and a negative activation entropy. To account for these observations, we may consider the totality of reasonable resonance structures which might be written for the ion $C^=$ in the initial and transition states. The transition state may be written as 14, wherein numerous of the resonance forms of the types given for the intermediates are implied.



(14)

The result of comparing the initial and transition states is that there appears to be in the transition state an over-all localization of a negative charge in the neighborhood of the departing nitrite group, whereas initially the two charges were dispersed throughout virtually the entire system. This concentration of charge may be facilitated by an increase in ionic strength. Further, the increased solvent orientation involved in the charge localization of such an activation process might lead to a negative entropy of activation.

Epstein and Winkler (ref. 3) report an activation energy of 14 kcal./mole for the reaction of RDX with sodium hydroxide in aqueous acetone. From their results, $\Delta S^{\ddagger}$, at 15.5°, is -14 e.u.[12] These quantities are much lower than the values reported here, and their rate constants are considerably higher. For example, they report a rate constant of 21.8 l. (mole min.)$^{-1}$ at 15.5°, while the result in this work for k_1 at 20.56° is 0.1006 l. (mole min.)$^{-1}$. Unfortunately, few details of their kinetic investigations are given, and it is difficult to compare results. The differences in rate constants may be largely a solvent effect, for we have noted that the decomposition is much more rapid in aqueous dioxane, for example, than in methanol.[23] On the other hand, it seems possible that the important nucleophilic agent in methanolic KOH is methoxide ion, in view of the fact that methanol is more acidic than water.[24] Hence the small difference in rate constants observed here for methanolic solutions of KOH and $NaOCH_3$ is probably less than the true difference in rate between (OH^-) and (OCH_3^-). The difference in basicity of the two ions may account in part for the considerable decrease in reaction rate on going to methanol from aqueous dioxane or aqueous acetone.

Experimental

Chemicals.—Commercial RDX was recrystallized several times from acetone; m.p. 203.8° dec. on the Fisher–Johns apparatus. Reagent grade chemicals were used without further purification except that in some cases the best available commercial anhydrous sodium perchlorate was recrystallized from methanol; the purified salt gave results identical with those obtained with the original material. The

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[17] There is evidence that the canonical form $>\overset{+}{N}=\overset{+}{N}<^{O^-}_{O^-}$ is an important contribution to the resonance hybrid of nitramines: L. E. Sutton, *J. Chem. Soc.*, 551 (1940); W. Costain and E. G. Cox, *Nature*, **160**, 826 (1947).

[18] At high temperatures, *a/b* values, and ionic strength, it was possible to obtain nearly quantitatively a third mole of nitrite from the RDX molecule, and according to the proposed scheme this would result in the formation of *s*-triazine or its decomposition products. The rate of production of the third nitrite was negligible kinetically.

[19] E. L. Holmes and C. K. Ingold, *J. Chem. Soc.*, 1305 (1926).

[20] J. W. Baker and D. M. Easty, *ibid.*, 1193, 1208 (1952).

[21] S. I. Miller and R. M. Noyes, THIS JOURNAL, **74**, 629 (1952).

[22] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[23] When the reaction was carried out in this solvent, an unidentified transient bright yellow color was observed at high *a/b* values which did not appear in methanol experiments. The color was immediately destroyed on the addition of mineral acid. It might be very tentatively suggested that this color represents a greater buildup of the intermediate B^- in this solvent. Similar stoichiometric results obtained in the two systems.

[24] J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

lithium and sodium methoxide solutions were prepared from methanol and the metals; the latter were first scraped clean under inert solvents and rinsed with several baths of methanol.

Distilled water was redistilled from alkaline permanganate. Commercial absolute methanol was used in most of the kinetic runs. In a few cases this solvent was carefully dried[25] and fractionated, but this procedure had no detectable effect on the rate constants. Commercial dioxane was purified by a standard procedure.[26]

Thermoregulation.—Commercial thermoregulators were used in ethylene glycol constant temperature baths. Temperatures were measured with a National Bureau of Standards platinum resistance thermometer and regulation was ±0.02° or better.

Determination of Nitrite.—A chloramine-T procedure[27] was adapted to the determination of methanolic nitrite. Use of this procedure was complicated in the present instance by the fact that the oxidation of nitrite is not instantaneous, requiring several minutes at room temperature, and during this time there is a slow oxidation of methanol. When, however, the analytical sample was diluted with 3.5 times its volume of water and allowed to stand exactly five minutes before the addition of the potassium iodide, the nitrite was quantitatively oxidized with negligible methanol decomposition.[28]

Because of the methanol reaction, the possible instability of aqueous chloramine-T even when stored in the dark,[27c] and the variable temperatures of the analytical aliquots, "blanks" were analyzed before each run instead of using a predetermined chloramine-T normality. A "blank" determination consisted in using an aliquot volume of pure methanol rather than the nitrite solution. The nitrite concentration was then calculated from the volume difference.

In testing this analysis, methanolic and aqueous solutions of commercial analytical reagent sodium nitrite gave experimentally identical results which agreed with the assay reported by the manufacturer. If standard aqueous nitrite were prepared from $AgNO_2$ and NaCl,[29] quantitative results were obtainable when the analysis was run on a macro scale. Over the range of concentrations encountered in a kinetic run, however, the average error was about 2%. The analysis was not affected by the presence of RDX or $NaClO_4$. Added formaldehyde or formic acid, reported products of the RDX decomposition, also had no effect. Alkaline and neutral methanolic nitrite solutions showed no decomposition under the conditions of the kinetic experiments. Nitrite ion itself did not react with RDX.

Alkali Determinations.—Potassium acid phthalate was used as the primary standard in the acid-base determinations, and when necessary the titrations in aqueous methanol were corrected for indicator blanks. Added nitrite had no significant effect on the determinations.

Polarographic Analysis for RDX.—In buffered methanol solution RDX gave at least three polarographic waves in the voltage range 0 to −2 (*versus* the saturated aqueous calomel electrode). On treatment of RDX solutions with alkali all three waves decreased in height, but only the first decreased progressively to zero. The rate of decrease of the later two was less than that of the first, and this was shown to be the result of the reduction of nitrite. The first wave was not influenced by the addition of nitrite and its height was, over the range of RDX molarity encountered, linear with concentration. The decrease in height to zero of the first wave was regarded as evidence that the organic decomposition products were not interfering with this RDX analysis. The latter point was not strictly proved, of course, in the absence of the isolation of intermediates; the agreement of the RDX stoichiometry and kinetics with the other analytical methods may, however, be cited as supporting evidence.

Polarograph.—A Leeds and Northrup automatically recording instrument, the Electro-Chemograph Type E, was employed. Polarographic cells were made from 40-ml. centrifuge tubes with a capillary inlet attached to the bottom from deoxygenation. Commercial water-pumped nitrogen was saturated with methanol and passed through the test solutions for one hour prior to analysis. This exceptionally long period was necessary for removal of the oxygen wave; that methanol solutions require long periods for deoxygenation has been reported previously.[30] The cell was connected to the calomel electrode by means of a saturated potassium chloride agar bridge.

The capillary was a section of 58 μ Corning marine barometer tubing with the characteristics (0.1 *N* aqueous KCl, −0.90 v. (S.C.E.), 40 cm. head of mercury, 30.1 ± 0.1°): t = 4.835 sec., $m^{2/3}t^{1/6}$ = 1.650 mg.$^{2/3}$ sec.$^{-1/2}$.

Diffusion Current Measurement.—The RDX wave appeared to be slightly better defined at weakly alkaline *p*H and in the presence of a maximum suppressor, although the effects of these variables were not studied in detail. In the analytical procedure adopted, acid fuchsin was added and a slightly alkaline buffer was used. The alkalinity was not great enough to cause perceptible destruction of the RDX wave over a period of several weeks at room temperature.

A limiting current was not well-defined, the first wave merging with the second and giving an inflection in the current-voltage diagram. After some practice, however, it was possible to select this inflection point quite reproducibly and an accuracy typical of polarographic methods was obtainable.

Apparent maximum currents were used,[31] the residual current extrapolated, and the vertical distance from this line to the inflection point used as a measure of the diffusion current. The "zero-damping" position was used down to RDX concentrations of 2×10^{-4} *M;* below this a "position 1" setting was necessary to get the entire wave on the chart at the necessary sensitivity. In the overlapping concentration region, diffusion currents measured at the two damping positions were identical.

Over the RDX concentration range 3×10^{-5} to 6×10^{-4} *M*, the empirical equation 15, applicable at 30.14 ± 0.1°, was derived.

$$(R) = 9.31 \times 10^{-5}(I - 0.08) \qquad (15)$$

Here I is the diffusion current in microamperes. From the standard deviation of the least squares slope[9] of 15, the error was estimated to be ±2.5%.

Half-wave Potential.—The half-wave potential was determined by the method recommended by the manufacturer,[32] *i.e.*, as the mean of values for the forward- and reverse-polarization waves. This procedure was found to give results for known compounds in satisfactory agreement with literature values. Once the diffusion current had been estimated, the half-wave potential was evaluated by plotting log $(I/I_d - I)$ *vs.* E and interpolating E at the point where the logarithm vanished; it was also found as the intersection with the wave of a line drawn parallel to the residual current line at half the wave height.[33] The two methods gave identical values for the half-wave potential, which, from 25 measurements used for the calibration, was −0.811 v. (S.C.E.), standard error of mean 0.001.[34] This is corrected for the *IR* drop through the cell and circuit. The resistance was measured after each polarogram with an Industrial Instruments, Inc., a.c. conductivity bridge; it was not allowed to exceed 2500 ohms.

Buffer and Supporting Electrolyte.—A stock solution of borate buffer in methanol was prepared in proportions corresponding to those given by Clark and Lubs for *p*H 8.0 in the

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(25) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 360.

(26) Reference 25, page 369.

(27) (a) E. D. Hughes, C. K. Ingold and R. I. Reed, *J. Chem. Soc.*, 2440 (1950). Chloramine-T was originally used as a reagent for nitrite by (b) P. N. VanEck, *Pharm. Weekblad*, **63**, 1117 (1926); *C. A.*, **20**, 3660 (1926). The method is reviewed in (c) F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 316.

(28) The time is of course dependent upon the (chloramine-T)/(NO_2^-) mole ratio, and as given is for approximately 0.1 *N* chloramine-T and 0.04 (or less) *N* $(NO_2)^-$. The methanol is sufficiently dilute in this procedure that it does not interfere with the starch-iodine color.

(29) F. D. Snell and F. M. Biffen, "Commercial Methods of Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1944, p. 237.

(30) P. Arthur and H. Lyons, *Anal. Chem.*, **24**, 1422 (1952).

(31) *Cf.* D. N. Hume, D. D. DeFord and G. C. B. Cave, THIS JOURNAL, **73**, 5323 (1951).

(32) Leeds and Northrup Catalog EM9-90 (1), 1950.

(33) O. H. Müller, "The Polarographic Method of Analysis," Chemical Education Publishing Co., Easton, Pa., 1951, Chapters IV and VII.

(34) This is apparently the first value reported for the reduction of a nitramine.

aqueous system.[35] Potassium rather than sodium hydroxide was used, and 0.5 *M* lithium chloride was the supporting electrolyte. A very small quantity of a precipitate of undetermined composition appeared on mixing these buffer components; it was allowed to settle and the supernatant liquid had a *p*H, with the glass electrode, of 7.4. This *p*H did not change perceptibly on dilution of the buffer with the alkaline reaction samples. The buffer capacity was relatively high, the acidic form having a concentration about 100 times that of the RDX; this was probably adequate to buffer the electrode reactions.[36]

Analytical Procedure.—Ten-ml. aliquot portions of the reaction solutions were diluted to 100 ml. with buffer and the samples analyzed in triplicate. To each test solution was added four drops of 0.05% methanolic acid fuchsin. The calculated RDX concentration was corrected to the original temperature of the reaction by means of the known temperature dependence of methanol density.[37]

General Techniques in Rate Runs.—For the very slow runs the reaction solutions were sealed in glass ampoules initially, allowed to come to temperature in the thermostated bath, and the concentrations and time obtained at the first titration used as the initial point in the calculation of rate constants. For the more rapid cases the appropriate quantity of base solution was sealed in an ampoule, this ampoule and a volumetric flask containing the RDX solution were allowed to come to temperature, and at zero time the ampoule was broken and the two solutions mixed and shaken vigorously. The nature of the reaction was such that it was very rapid initially and then slow as (largely) k_2 governed the kinetics. Hence after the rate had slowed appreciably the reaction solutions were transferred rapidly to ampoules in order that evaporation losses be minimized. This operation gave no "breaks" in the smoothness of the concentration-time curves, and no correction in time appeared necessary.

Times of reaction were taken when a constant fraction (approximately half) of the aliquot sample had been added to the acid solution (or, in the case of phenolphthalein alkalimetry, to cold water) which arrested the reaction.

The microburets and automatic pipets which were used were calibrated with the appropriate solvents.

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[35] N. A. Lange, "Handbook of Chemistry," Sixth Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1103.

[36] Reference 33, page 112.

[37] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 27.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A Kinetic Study of the Diborane-Ethylene Reaction[1]

BY ALFRED T. WHATLEY AND ROBERT N. PEASE

RECEIVED AUGUST 10, 1953

The combination of ethylene with diborane yielding boron triethyl as a final product proceeds in the range 120–175° at a rate given by $-dp/dt = k[B_2H_6]^{3/2}/(1 - a[B_2H_6]/[C_2H_4])$. As the equation indicates, the reaction becomes mildly explosive when the B_2H_6/C_2H_4 ratio is sufficiently increased (beyond about 0.5); and the excess of diborane is consumed in the process. A mechanism of ethylene addition is proposed.

Hurd[2] has reported that diborane reacts slowly with excess of ethylene at 100° to yield mainly boron triethyl. Since the process inevitably involves breakage of the boron–boron bond at some stage, it was of interest to determine whether the kinetics would reveal a fractional order in diborane such as has been observed in the decomposition of diborane[3] and in other reactions.

Our curiosity about the diborane–ethylene reaction was further heightened by some observations made in the course of experiments on diborane–oxygen explosions.[4] Such explosions occur after an induction period at 100° and above, within a range of diborane–oxygen compositions. Since it had been shown that low concentrations of boron triethyl react explosively with oxygen at 0°,[5] it had been presumed that addition of ethylene to diborane–oxygen mixtures would enhance the explosibility of the latter *via* initial formation of boron triethyl. However, this did not prove to be the case. On the contrary, ethylene acted as an inhibitor. A partial explanation came from the observation that when an ethylene–diborane mixture in the ratio 2:1 or less[6] was admitted to the hot reaction flask, the pressure first fell and then rose abruptly due apparently to decomposition of a portion of the excess diborane with liberation of hydrogen. Thus, whatever the full explanation of the inhibiting effect of ethylene on the diborane–oxygen explosions might be, it was clear that the reaction of diborane with ethylene alone merited study.

Experimental

Diborane was prepared in the laboratory, and purified by freezing with liquid nitrogen and pumping off any hydrogen present, followed by distillation of the diborane from a melting *n*-butane bath (−135°). At this temperature none of the other boranes has an appreciable vapor pressure. Analysis by hydrolysis indicated less than 2% impurities. The ethylene used was obtained from the Matheson Com-

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[2] D. T. Hurd, THIS JOURNAL, **70**, 2053 (1948).

[3] J. K. Bragg, L. V. McCarty and F. J. Norton, *ibid.*, **73**, 2134 (1951); R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951).

[4] To be reported. See F. P. Price, *ibid.*, **72**, 5361 (1950).

[5] R. S. Brokaw, E. J. Badin and R. N. Pease, *ibid.*, **70**, 1921 (1948).

[6] The stoichiometric mixture for boron triethyl as product is 6:1.