161° dec. Recrystallization from benzene gave yellow-orange crystals, m.p. 161° dec. Infrared spectra of the product both in potassium bromide disk and in chloroform solution showed a broad band at 3.14 μ and a single, sharp band at 4.54 μ.

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61; mol. wt., 222.236. Found: C, 75.94; H, 4.62; N, 12.82; mol. wt.,[11] 223.

A sample of the product was also submitted for nuclear magnetic resonance studies[8] made at a frequency of 60 mc. in hexadeuterated acetone solution. An oxime hydrogen peak was found at −274 c.p.s. (relative to benzene in an external annulus). A phenyl hydrogen peak appeared at −23 c.p.s. A family of peaks ranging from about −4 to +33 c.p.s. was attributed to quinoid hydrogen. Under the conditions of the studies, a hydrogen attached to a tertiary carbon atom should have produced a peak in the region of +70 to +100 c.p.s. No peak distinguishable from noise was found in this region.

p-Chlorophenylcyanomethylenequinone Oxime.—Following a similar procedure, 21.20 g. of *p*-chlorobenzyl cyanide and 15.38 g. of nitrobenzene gave 24.8 (77% yield) of the quinone oxime, m.p. 188–189° dec. Recrystallization from benzene gave yellow needles, m.p. 195° dec. The infrared spectrum of the product in a potassium bromide disk showed a broad band at 3.14 μ and a single, sharp band at 4.54 μ.

Anal. Calcd. for $C_{14}H_9N_2ClO$: C, 65.60; H, 3.53; N, 10.92; Cl, 13.81. Found: C, 65.46; H, 3.58; N, 10.72; Cl, 13.56.

p-Methoxyphenylcyanomethylenequinone Oxime.—In like manner, 10.3 g. of *p*-methoxybenzyl cyanide and 7.86 g. of nitrobenzene gave 12.3 g. (77% yield) of the quinone oxime, m.p. 161° dec. Recrystallization from benzene gave yellow-orange needles, m.p. 161° dec. The infrared spectrum of the oxime in a potassium bromide disk showed a broad band at 3.20 μ and a single, sharp band at 4.54 μ.

Anal. Calcd. for $C_{15}H_{12}N_2O$: C 71.41; H, 4.79; N, 11.11. Found: C, 71.71; H, 5.04; N, 11.12.

α-Naphthylcyanomethylenequinone Oxime.—In the usual manner, 5.85 g. of α-naphthylacetonitrile and 3.93 g. of nitrobenzene produced 5.7 g. (65% yield) of the quinone oxime, m.p. 165° dec. Two recrystallizations from benzene gave yellow crystals, m.p. 169° dec. The infrared spectrum of the quinone oxime in a potassium bromide disk showed a broad band at 3.15 μ and a single, sharp band at 4.53 μ.

Anal. Calcd. for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.67; H, 4.57; N, 10.40.

Oxidation of Phenylcyanomethylenequinone Oxime.—To a solution of 30 g. of potassium hydroxide (assay 85%) in 300 ml. of water was added 11.0 g. of the quinone oxime. The mixture was stirred until all the solid dissolved, producing a deep-red solution. To this solution was added 60 g. of 30% hydrogen peroxide in 140 ml. of water. The reaction mixture was allowed to stand at room temperature for 3 hours during which time a tan solid precipitated. The solid, *p*-nitrobenzophenone, was collected by filtration, washed with water and dried; weight 6.50 g., m.p. 110–120°. After two recrystallizations from ethanol–water: m.p. 137–138° (lit.[12] 138°); phenylhydrazone, m.p. 149–150° (lit.[13] 142°).

Anal. Calcd. for phenylhydrazone $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.59; H, 4.71; N, 13.35.

Oxidation of p-Chlorophenylcyanomethylenequinone Oxime.—In similar manner 12.83 g. of the quinone oxime produced 11.0 g. of crude *p*-nitrophenyl *p*-chlorophenyl ketone, m.p. 90–94°; recrystallized from ethanol, m.p. 100–101° (lit.[14] 98°); phenylhydrazone, m.p. 204–206°.

Anal. Calcd. for $C_{19}H_{14}N_3O_2Cl$: C, 64.87; H, 4.01; N, 11.95. Found: C, 64.76; H, 4.24; N, 11.92.

Oxidation of p-Methoxyphenylcyanomethylenequinone Oxime.—In like manner 15 g. of the quinone oxime produced 9.4 g. of crude *p*-nitrophenyl *p*-methoxyphenyl ketone, m.p. 116–118°; recrystallized from methanol–water, m.p. 121–123° (lit.[15,16] 121°); 2,4-dinitrophenylhydrazone, m.p. 265–266° dec. (lit.[16] 265° dec.).

NOTRE DAME, IND.

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[11] Molecular weight determined by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[12] G. Schroeter, *Ber.*, **42**, 3356 (1909).

[13] P. Carre, *Compt. rend.*, **144**, 34 (1907).

[14] J. Boeseken, *Rec. trav. chim.*, **23**, 107 (1904).

[15] K. Auwers, *Ber.*, **36**, 3899 (1903).

[16] H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 529 (1951).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Mechanism of the Decomposition of 1,1,1,3-Tetranitro-2-phenylpropane to Nitroform and β-Nitrostyrene

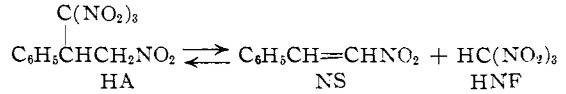
BY JACK HINE AND LLOYD A. KAPLAN

RECEIVED SEPTEMBER 29, 1959

The kinetics of the decomposition of 1,1,1,3-tetranitro-2-phenylpropane to nitroform and β-nitrostyrene in methanol solution have been studied in the presence of hydrogen chloride and of pyridine–pyridine hydrochloride buffers. The reaction was found to be subject to general base catalysis. The reaction mechanism appears to involve the removal of a proton by a base to give the 1,1,1,3-tetranitro-2-phenyl-3-propyl anion which then loses the nitroform (trinitromethyl) anion to give β-nitrostyrene. In strongly acidic solutions the decomposition of the intermediate carbanion is the rate-controlling step of the reaction, while in the pyridine-buffered solutions the carbanion formation is rate controlling. Although the reverse reaction, the addition of nitroform to β-nitrostyrene, can be studied only with considerably less accuracy, its rate was found to be essentially equal to that predicted from the equilibrium constant and the decomposition rate measurements made under non-equilibrium conditions. This observation shows that the undissociated nitroform molecule is probably not important as a proton donor in the rate-controlling step of the addition reaction.

Introduction

While qualitative observations and analogies with more carefully studied reactions may be used to suggest quite plausible mechanisms for the Michael reaction and its reversal, only a few kinetic studies have been reported.[1] It was felt that further kinetic studies would be desirable to learn more about which step of the reaction is rate controlling under various conditions. We have accordingly studied the decomposition of 1,1,1,3-tetranitro-2-phenylpropane (HA) and of the reverse reaction, the addition of nitroform (HNF) to β-nitrostyrene (NS).



$$C_6H_5CH(C(NO_2)_3)CH_2NO_2 \rightleftharpoons C_6H_5CH{=}CHNO_2 + HC(NO_2)_3$$

HA NS HNF

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[1] *Cf.* W. J. Jones, *J. Chem. Soc.*, **105**, 1547 (1914); M. J. Kamlet and D. J. Glover, THIS JOURNAL, **78**, 4556 (1956); Y. Ogata, M. Okano, Y. Furuya and I. Tabushi, *ibid.*, **78**, 5426 (1956).

Results and Discussion

Preliminary studies showed that at room temperature HA dissociated at a negligible rate in hexane, very slowly in ether, somewhat faster in dioxane, and much more rapidly in methanol. While the reaction in pure methanol was initially quite rapid, being observable within a few seconds at 25°, it became much slower as the reaction proceeded, presumably because the liberated nitroform increased the acidity of the solution. This presumption was supported by the observation that in a methanol solution 0.004 M in HCl, less than 3% decomposition occurred in 19 hours at 25°.

The Decomposition of HA in Methanolic HCl Solution.—In order to learn more about the effect of acidity on the reaction rate, kinetic studies were carried out in the presence of three different concentrations of HCl in methanol. The reaction was conveniently followed by spectrophotometric measurements since β-nitrostyrene has an absorption maximum at 3100 Å. and the nitroform anion has one at 3500 Å., whereas HA and nitroform do not absorb appreciably above 3000 Å. From these measurements and the ionization constant of nitroform that we determined independently, the extent of reaction could be calculated. In each run satisfactory first-order rate constants were obtained. The values are listed in Table I.

TABLE I

RATES OF DECOMPOSITION OF 1,1,1,3-TETRANITRO-2-PHENYLPROPANE IN METHANOLIC HCl AT 40°

[HCl]	10^7k, sec.$^{-1}$
0.0903	6.28 ± 0.14
.0221[a]	9.53 ± .19
.0048[a]	11.69 ± .39

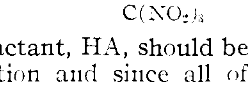
[a] Sodium perchlorate added to bring the ionic strength to 0.10.

It seems to us that the only plausible reaction mechanism involves the removal of a proton on the same carbon as a nitro group and the loss of the trinitromethyl group as an anion. This, of course, is simply the reverse of the usual mechanism for the Michael reaction.[2] If this mechanism is considered as occurring by two separate steps with a carbanion as an intermediate, then, since methanol and methoxide ions are the only species present likely to perform the initial proton removal to an appreciable extent, the following mechanism may be written

$$HA + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + MeOH$$

$$HA + MeOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^- + MeOH_2^+$$

$$A^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NS + NF^-$$



$$A^- \text{ is } C_6H_5CH\overset{-}{C}HNO_2 \text{ with } C(NO_2)_3 \text{ below the first CH}$$

Since the reactant, HA, should be a *weak* acid in methanol solution and since all of our measurements have been carried out in solutions that are at least somewhat acidic, we may make the steady state approximation for the anion, A^-. Neglecting k_{-3}, since the reaction is essentially irreversible at the concentrations employed in the runs under consideration, this leads to the rate equation

$$v = \frac{(k_1[MeO^-] + k_2)k_3[HA]}{k_{-1} + k_{-2}[H^+] + k_3} \qquad (1)$$

where k_{-1} and k_2 have been treated as first-order rate constants. Not all of the rate constants used are independent, however. From the principle of microscopic reversibility[3] it follows that

$$k_{-1} = k_1k_{-2}K_M/k_2 \qquad (2)$$

where K_M is the autoprotolysis constant of methanol. After the substitution of eq. 2 in eq. 1 and rearrangement of terms it is seen that the observed first-order rate constants (k) for the decomposition of HA have the meaning

$$k = \frac{(k_1K_M/[H^+]) + k_2}{r_2\left(\frac{k_1K_M}{k_2} + [H^+]\right) + 1}$$

where $r_2 = k_{-2}/k_3$.

Since three k's were determined at three different acidities we may solve the three simultaneous equations[4] that may be written, for the three unknowns, r_2, k_2 and k_1. The values obtained are

$r_2 = 8.66$ l. mole^{-1}
$k_2 = 1.12 \times 10^{-6}$ sec.$^{-1}$
$k_1 = 4.75 \times 10^{6}$ l. mole^{-1} sec.$^{-1}$

From these results it may be calculated that in the runs for which data are given in Table I, from 91.4 to 99.5% of the initial proton removal is due to methanol rather than methoxide ions. Thus the principal reason that the reaction rate increases with decreasing acidity is not because there are more methoxide ions present but because there are fewer methyloxonium ions to divert A^- ions from transformation to the final products. As might be expected from the relative unimportance of proton removal by methoxide ions, the reliability of the value calculated for k_1 is quite low. In fact, if k_1 is completely neglected, the optimum values of k_2 and r_2 (1.19×10^{-6} sec.$^{-1}$ and 10 l. mole^{-1}) calculated by the method of least squares are capable of reproducing the values of k listed in Table I with an average deviation of 1.8%. As will be shown in the subsequent section, studies in pyridine buffers show that k_1 is actually quite small and may be neglected for the runs listed in Table I.

The Decomposition of HA in the Presence of Methanolic Pyridine Buffers.—It seemed probable that useful additional information could be obtained by studying the reaction under more basic conditions where we would expect the initial proton

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(2) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 694.

(3) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 202.

(4) The value of pK_M (16.66) of Bjerrum, Unmack and Zechmeister[5] was corrected to 15.97 for use at ionic strength 0.1 by the assumption that changing ionic strength has the same effect on K_M as we have observed it to have on the ionization of nitroform, a reaction of the same charge type. Not having available any data on the temperature dependence of K_M we used this value over the whole temperature range, 25-40°. The only rate constant whose value is dependent on the value of K_M used is k_1.

(5) N. Bjerrum, A. Unmack and L. Zechmeister, *Kgl. Danske Videnskab. Math. fys. Medd.*, **5**, No. 11 (1925); *C. A.*, **19**, 3196 (1925).

removal to become completely rate controlling (since even in the presence of 0.0048 *M* HCl more than 90% of the intermediate carbanions appear to be transformed directly to the final products). We therefore studied the reaction in the presence of a pyridine–pyridine hydrochloride buffer. Under these conditions the additional reaction path

$$HA + C_5H_5N \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A^- + C_5H_5NH^+$$

becomes possible for the formation of the intermediate anion. The rate equation may now be written

$$v = \frac{(k_1[MeO^-] + k_2 + k_4[C_5H_5N])k_3[HA]}{k_{-1} + k_{-2}[H^+] + k_{-4}[C_5H_5NH^+] + k_3} \quad (3)$$

From the values previously obtained for r_2 and k_{-1}/k_3 [this is simply equal to $r_2(k_1K_M/k_2)$] it may be seen that k_{-1} and $k_{-2}[H^+]$ may be neglected in comparison to k_3 in the denominator of eq. 3 for application to our studies in pyridine buffers where $[H^+]$ is at all times below 10^{-5} *M*. Since the principle of microscopic reversibility may be applied to the present case to show that

$$k_{-4} = \frac{k_{-2}k_4K_{PH^+}}{k_2}$$

where K_{PH^+} is the acidity constant of the pyridinium ion in methanol, the first-order rate constant for the decomposition of HA in pyridine buffers should have the form

$$k = \frac{k_1[MeO^-] + k_2 + k_4[C_5H_5N]}{(k_4/k_2)r_2[C_5H_5NH^+]K_{PH^+} + 1} \quad (4)$$

The reaction was found experimentally to be first order in HA in any given run (in all cases the buffer concentration was much larger than that of HA) and the first-order rate constants obtained in the presence of various buffer concentrations and ratios are listed in Table II.

TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF HA IN METHANOLIC PYRIDINE BUFFERS[a]

Temp., °C.	$10^3[C_6H_5N]$	$10^3[C_5H_5NH^+]$	10^5k, sec.$^{-1}$
25.0	4.141	4.147	3.58 ± 0.02[b]
25.0	2.455	1.228	2.40 ± .12
25.0	4.910	2.456	4.68 ± .10
25.0	9.076	3.025	7.67 ± .05
25.0	18.15	6.050	15.35 ± .47
38.0	2.046	0.682	5.18 ± .13
38.0	3.758	1.698	8.97 ± .14
38.0	4.163	1.387	9.53 ± .05

[a] Sodium perchlorate added to keep the ionic strength at 0.1 in all cases. [b] Average deviation.

It is seen that at a constant $[C_5H_5N]/[C_5H_5NH^+]$ ratio and hence a constant methoxide ion concentration, the pseudo first-order rate constant is almost proportional to the concentration of pyridine. This shows that the principal term in the numerator of eq. 4 is $k_4[C_5H_5N]$ and the principal term in the denominator is unity; that is, the relation

$$k = k_4[C_5H_5N]$$

is approximately true. From this approximate relation k_4 may be calculated to be about 8 × 10^{-3} at 25° and 22 × 10^{-3} at 38°. From these values of k_4, the term $r_2k_4K_{PH^+}/k_2$ in the denominator of eq. 4 may be calculated[6] to be about 6 × 10^{-8} at 40° (and relatively insensitive to temperature since the rate constants appear only as ratios). Hence the entire first term in the denominator of eq. 4 may be neglected and the expression may be reduced to the form

$$k = k_1[MeO^-] + k_2 + k_4[C_5H_5N] \quad (5)$$

From the values of *k* in Table II it is clear that the optimum (but as stated, relatively unreliable) value of k_1 calculated from the *k*'s obtained in HCl solution is far too large. Values of k_2 of 4 × 10^{-7} and 10 × 10^{-7} at 25° and 38°, respectively, were estimated from the value at 40° and the assumption that the activation energy for k_2 is the same as for k_4. Since k_2 is quite a minor term in eq. 5, errors in this estimate will have little effect on the values calculated for k_1 and k_4. Optimum values of k_1 and k_4 were then calculated from the data of Table II by the method of least squares. The resulting k_1 values of 5.2 × 10^4 and 5.1 × 10^4 l. mole^{-1} sec.$^{-1}$ at 25° and 38° and k_4 values of 8.10 × 10^{-3} and 2.19 × 10^{-2} l. mole^{-1} sec.$^{-1}$ are capable of reproducing the *k*'s of Table II with an average deviation of less than 2%. The fact that k_1 has a higher value at 25° than at 38° may suggest an error in our interpretation of our results. However, in addition to the fact that the k_1 values are uncertain because so small a fraction of the reaction is brought about by methoxide ion, the value of k_1 at 38° is subject to the near-certainty of error in our assumptions that K_M and K_{PH^+} are temperature independent. While such an error would create a proportionate error in k_1 at 38° it would have no effect on the degree to which our *k* values can be fit by eq. 5. We believe that the contribution of the k_1 term in the case of the pyridine-catalyzed reaction is probably real, since if k_1 is completely neglected the optimum values of k_4 and the values estimated for k_2 cannot correlate the *k*'s values obtained to within any better than a 5% average deviation.

The Addition of Nitroform to β-Nitrostyrene.—In order to provide more information about the reverse reaction, the addition of HNF to NS, the equilibrium constant, K_e, was determined.

$$K_e = [HNF]_e[NS]_e/[HA]_e$$

The method of approach from both sides, as illustrated in Fig. 1, gave

$$\log K_e^{40°} = -1.20 \pm 0.03 \text{ or } K_e^{40°} = 0.063 \pm 0.004$$

The establishment of K_e permits a determination of the value of an additional rate constant, k_{-3}, since

$$\frac{k_2k_3}{k_{-2}k_{-3}} = \frac{[NS]_e[MeOH_2^+]_e[NF^-]_e}{[HA]_e}$$

$$k_{-3} = \frac{k_2}{r_2K_eK_N} = 3.23 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1} \text{ at } 40°$$

where K_N is the ionization constant of nitroform.

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(6) The value 5.55 used for pK_{PH^+} had been determined at 25°,[7] but we have used it at 38° also since no data on the effect of temperature seemed available and since the ionization constants of some amines have been found to increase with temperature while others decrease.[8] This assumption of the temperature independence of K_{PH^+} has no effect on the value that we would calculate for any *k* except k_1.

(7) H. Goldschmidt and E. Mathieson, *Z. physik. Chem.*, **119**, 439 (1926).

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

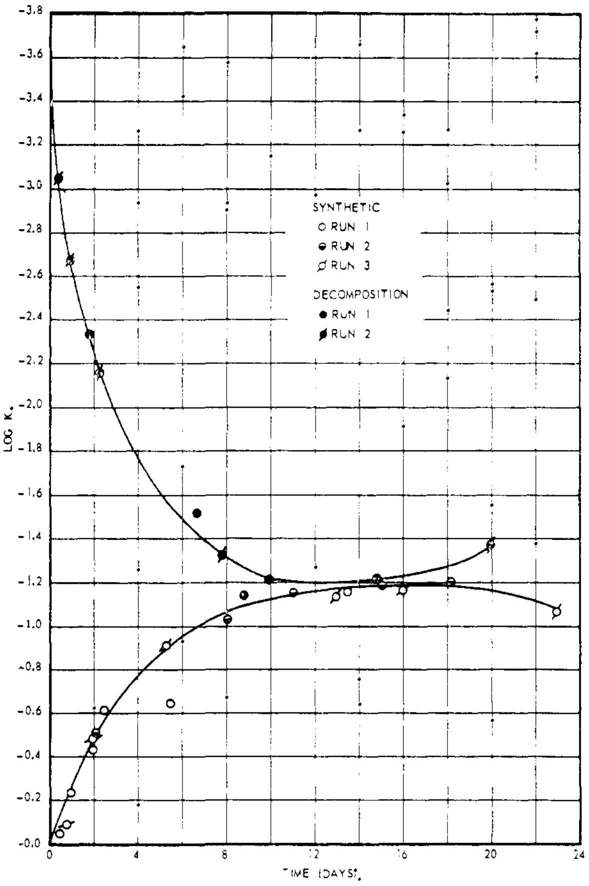

Fig. 1.—Plot of log K_e *versus* time at 40°.

The next measurements were made on the kinetics of the addition of HNF to NS. If the proposed reaction mechanism operates for the decomposition reaction it must, of course, also operate (in reverse) for the addition reaction. There is a new step that must be considered in the present case, however. This involves the possible entrance of nitroform and its anion into the reaction as a catalytic species.

$$\mathrm{HA} + \mathrm{NF}^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{A}^- + \mathrm{HNF}$$

In the decomposition reactions, which were all run in quite dilute solution, the concentration of nitroform and its anion never reached a level where the significant contribution of the step shown above seems at all plausible. From the study of the decomposition reaction, it is clear that at hydrogen ion concentrations greater than about 0.001 *M*, as in all of the addition reactions studied, k_1 and k_{-1} may be neglected. Neglecting these terms for the addition reaction, too, the steady state approximation gives the relation

$$[\mathrm{A}^-] = \frac{k_2[\mathrm{HA}] + k_5[\mathrm{HA}][\mathrm{NF}^-] + k_{-3}[\mathrm{NS}][\mathrm{NF}^-]}{k_{-2}[\mathrm{MeOH_2}^+] + k_{-5}[\mathrm{HNF}] + k_3}$$

Therefore, the *net* forward reaction rate may be expressed

$$\frac{\mathrm{d}[\mathrm{HA}]}{\mathrm{d}t} = \frac{(r_2k_{-3}K_{\mathrm{N}}[\mathrm{HNF}][\mathrm{NS}] - k_2[\mathrm{HA}])(1 + [\mathrm{NF}^-]k_5/k_2)}{r_2[\mathrm{MeOH_2}^+] + (k_{-5}/k_3)[\mathrm{HNF}] + 1} \qquad (6)$$

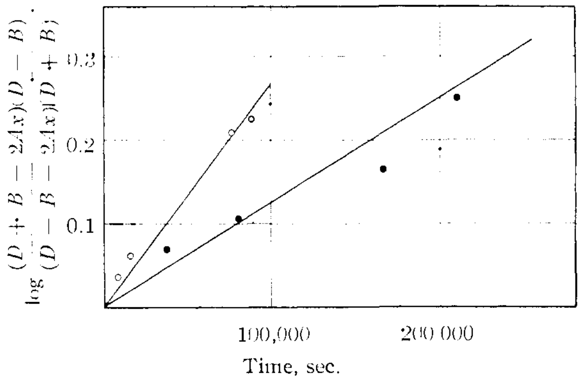

Fig. 2.—Kinetic plot for addition of nitroform to β-nitrostyrene.

Since the terms $[\mathrm{NF}^-]k_5/k_2$, $r_2[\mathrm{MeOH_2}^+]$ and (k_{-5}/k_3) [HNF] are not too large compared to one, we may take the values of $[\mathrm{NF}^-]$, $[\mathrm{MeOH_2}^+]$ and [HNF] (in the denominator but not in the numerator) as their average values during a run. That is, in a given run we have a constant *C*.

$$C = \frac{1 + [\mathrm{NF}^-]k_5/k_2}{r_2[\mathrm{MeOH_2}^+] + (k_{-5}/k_3)[\mathrm{HNF}] + 1}$$

Calculations using the maximum possible value of k_{-5}/k_3, whose estimate is described below, show that *C* never varies from its average value by so much as 0.5% in our runs. If x = [HA] and a = $[\mathrm{HNF}]_0$ (this is the concentration of HNF actually present in the undissociated form, not the formal concentration) then the approximation [HNF] = $(a - x)$ is never in error by so much as 0.2% in our runs. With these approximations eq. 6 becomes

$$\mathrm{d}x/\mathrm{d}t = C[A(a - x)(b - x) - k_2x] \qquad (7)$$

where $A = r_2k_{-3}K_{\mathrm{N}}$ and $b = [\mathrm{NS}]_0$. Integration of eq. 7 gives

$$2.3 \log \frac{(D + B - 2Ax)(D - B)}{(D - B - 2Ax)(D + B)} = BCt \qquad (8)$$

where

$$B = \sqrt{A^2(a - b)^2 + 2k_2A(a + b) + k_2^2}$$
$$D = A(a + b) + k_2$$

Since k_4 and k_{-4} are found only in the constant *C*, a plot of the logarithmic term in eq. 8 *versus* time can be made without a knowledge of the value of these rate constants. From the values already determined for r_2, k_2, k_{-3} and K_{N} and the data on individual kinetic runs, such plots were made (see Fig. 2). The run represented by solid circles was carried out at an ionic strength of only about 4 × 10^{-3} (due to the ionized nitroform) rather than at 0.1 where r_2, k_2 and k_{-3} were determined. However, only reactions between ions should be greatly affected by the change in ionic strength. Only r_2 and K_{N} relate to reactions of this type and since they change in opposite directions their product should be relatively independent of the ionic strength. Since these terms appear only as in the r_2K_{N} product we have used at all ionic strengths the value for this product appropriate to ionic strength 0.1. Although the study of the addition reaction involved greater experimental uncertainties than that of the decomposition reaction, the points in Fig. 2 are seen to lie fairly near straight lines. The straight lines shown, however, were not chosen to fit the points but were calculated from eq. 8 on the assumption that the terms $[NF^-]k_5/k_2$ and $(k_{-5}/k_3)[HNF]$ are negligible. From the agreement observed it is believed that most of the reaction goes through the path governed by k_2 and k_{-2} and not more than one-fifth of it goes through the path governed by k_5 and k_{-5}. By expressing C in terms of known constants and k_5 it may be shown that k_5 may therefore be no larger than 2×10^{-5} l. mole^{-1} sec.$^{-1}$ at 40°.

The rate and equilibrium constants that we have determined in this investigation are listed in Table III. The values of k_{-1}, k_{-2}, k_3, k_{-4} and k_{-5}, the rate constants for reactions of the intermediate A^-, are also listed expressed in terms of K_{HA}, the ionization constant of HA as an acid in methanol. It should be possible to estimate K_{HA} within a few powers of ten by use of standard methods.[9]

TABLE III

SUMMARY OF RATE AND EQUILIBRIUM CONSTANTS

$k_1^{25°} \sim 5.2 \times 10^4$ l. mole^{-1} sec.$^{-1}$	$k_{-1} = k_1K_M/K_{HA}$
$k_1^{38°} \sim 5.1 \times 10^4$ l. mole^{-1} sec.$^{-1}$	$k_{-2} = k_2/K_{HA}$
$k_2^{40°} = 1.19 \times 10^{-6}$ sec.$^{-1}$	$k_3 = k_{-3}K_NK_e/K_{HA}$
$(k_{-2}/k_3)^{40°} = 10$ l. mole^{-1}	$k_{-4} = k_4K_{PH^+}/K_{HA}$
$k_4^{25°} = 8.10 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$	$k_{-5} = k_5K_N/K_{HA}$
$k_4^{38°} = 2.19 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$	$k_5^{40°} < 2 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$
$k_{-3}^{40°} = 3.23 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$	$K_e^{40°} = 0.063$ mole l.$^{-1}$

Rate Constants for Proton Removal from HA.—As an independent check on the reaction mechanism that we have proposed it is useful to consider whether the magnitudes of the k's listed in Table III are reasonable in view of what is known about the kinetics of related reactions. One relationship that at might first seem unexpected is that k_{-4}, the rate constant for the protonation of A^- by pyridinium ion, is said to be larger than k_{-5}, the rate constant for protonation by the 200-fold stronger acid, nitroform. However, this observation is in agreement with the generalization that acidic protons attached to carbon are donated to bases more slowly than equally acidic protons attached to oxygen or nitrogen. Thus, the ammonium ion ($pK \sim 10$) undergoes deuterium exchange in acidic aqueous solution at 0° [10] millions of times more rapidly than nitroethane ($pK \sim 8.6$) would under these conditions.[11] It is probable that steric hindrance is also of importance in decreasing the reactivity of nitroform.

The rate constants observed for the removal of a proton from nitroethane by various bases are: $k = 1.25 \times 10^{-7}$ sec.$^{-1}$ for water,[11] $k = 3.57 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ for pyridine,[12] $k = 8.04$ l. mole^{-1} sec.$^{-1}$ for hydroxide ions,[13] all in aqueous solution at 34.85°. Pearson and co-workers' observations that pyridine is 160,000 times as reactive as water (on an equal concentration basis) toward nitroethane compared to our observation that pyridine is 530,000 times as reactive as methanol toward HA (2-phenyl-2-trinitromethylnitroethane) is reasonable in view of the fact that water is a somewhat stronger base than methanol.[14] The relative magnitude of k_1 and the absolute magnitudes of all of our k's are believed to be in the general area expected, when the following factors are considered. Reactions like those governed by k_2 and k_4, in which there is charge formation in the transition state, should proceed more rapidly in water than in methanol.[15] Reactions like those of the hydroxide and methoxide ions with nitro compounds should be faster in methanol.[15] The methoxide ion is a slightly weaker base than the hydroxide ion.[16] Nitroethane must be a weaker acid than its electronegatively substituted derivative, HA.

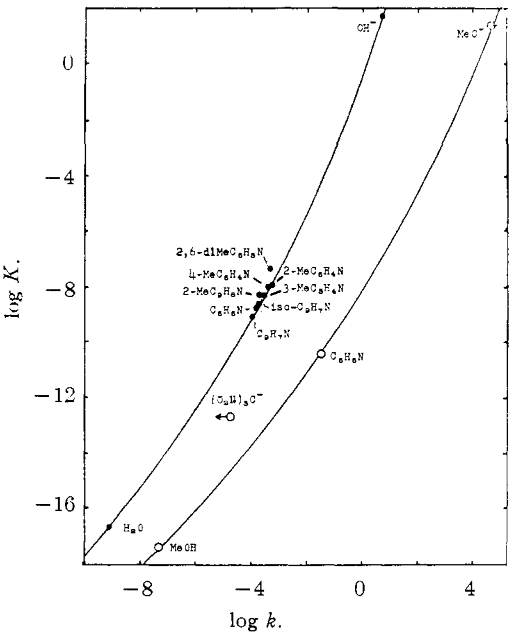

Fig. 3.—Brönsted-type plot of logs of basicity constants of bases *versus* logs of rate constants for proton removal from: solid circles, nitroethane in water[11−13]; open circles, 1,1,1,3-tetranitro-2-phenylpropane in methanol. The point with an arrow lies an unknown distance in the direction shown.

Figure 3 is a Brönsted-type plot of our rate constants for proton removal from HA by various bases at 40° (open circles) and data[11−13] on the rates of reaction of nitroethane with various bases in water at 25°. For some of the latter data it has been assumed that the various substituted pyridine bases will react 37% faster in pure water than in 30% ethanol just as pyridine does.[12] The values of K_b are defined

$$K_b = [BH^+][OH^-]/[B]$$

in water and analogously in methanol. The proper value of K_b for hydroxide ion is thus 55.5 and that of water is $K_w/55.5$ since pure water is 55.5 M.

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[9] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, chap. VI; R. W. Taft, Jr., "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

[10] A. I. Brodski and L. V. Sulima, *Doklady Akad. Nauk S. S. S. R.*, **74**, 513 (1950); *cf.* Louis Kaplan and K. E. Wilzbach, THIS JOURNAL, **76**, 2593 (1954); and C. G. Swain, J. T. McKnight, M. M. Labes and V. P. Kreiter, *ibid.*, **76**, 4243 (1954).

[11] R. G. Pearson and R. L. Dillon, *ibid.*, **72**, 3574 (1950).

[12] R. G. Pearson and F. V. Williams, *ibid.*, **75**, 3073 (1953).

[13] Extrapolated from the data of R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* (*London*), **A212**, 16 (1952).

[14] H. Goldschmidt and A. Thueson, *Z. physik. Chem.*, **81**, 30 (1912); H. Goldschmidt and P. Dahll, *ibid.*, **108**, 121 (1924).

[15] This follows from the theory of solvent effects described in ref. 2, Sec. 25. For specific supporting data see ref. 12.

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

Similarly K_b's for methoxide ion and methanol are 24.7 and $K_M/24.7$, respectively. Since neither set of data is fit well by a straight line, we have arbitrarily chosen the arc of a circle of the same radius to fit both sets of points (ignoring the point for nitroform) and found good agreement, as shown. We regard this as additional evidence in support of our reaction mechanism from which the interpretation of k_1, k_2 and k_4 as rate constants for removal of α-protons from a nitro compound arose.

The only rate constant determined with sufficient precision at two temperatures to warrant calculating activation parameters was k_4, for which we calculated $\Delta H^{\ddagger} = 13.5$ kcal./mole and $\Delta S^{\ddagger} = -16.8$ e.u. from the absolute rate equation[17]

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

A comparison of these data with those of Pearson and Williams[12] shows that the greater reactivity of HA than nitroethane toward pyridine is partly an entropy and partly an enthalpy effect.

Other Reaction Mechanisms.—There are other reaction mechanisms such as a concerted one-step E2 type[18] elimination reaction

$$\mathrm{HA} + \mathrm{B} \longrightarrow \mathrm{NS} + \mathrm{NF}^- + \mathrm{BH}^+$$

or a process in which the decomposition of A^- is acid catalyzed

$$\mathrm{HA} + \mathrm{B} \rightleftarrows \mathrm{A}^- + \mathrm{BH}^+$$

$$\mathrm{A}^- + \mathrm{BH}^+ \longrightarrow \mathrm{NS} + \mathrm{HNF} + \mathrm{B}$$

which explain the observed base catalysis but not the data of Table I. Thus the decomposition of HA has been shown to proceed *via* the rather unusual carbanion mechanism (E1cB[18]) for elimination. We plan to discuss this point further in connection with other examples in a subsequent paper.

Experimental

Preparation and Purification of Reagents.—Potassium nitroform was prepared from tetranitromethane by the method of Macbeth and Orr.[19] To liberate nitroform from its potassium salt, dry hydrogen chloride was passed into a stirred suspension of the salt in hexane until the original bright yellow color became a very pale yellow. Then dry nitrogen was bubbled through the mixture to remove the excess hydrogen chloride. The mixture was filtered and cooled in a Dry Ice-bath. The white crystalline nitroform that separated on cooling was collected on a filter with exclusion of moisture and then distilled at reduced pressure through a 9-cm. Vigreux column in an all-glass still. The material collected at 48–49° (15 mm.), crystallized at room temperature (25°) to a white solid that became yellow upon exposure to much atmospheric moisture. Only white material was used in these investigations. *All operations with nitroform and its salt were carried out with adequate precautions since both materials are explosive.*

Methanol was purified by the method of Vogel.[20] Pyridine was fractionated over potassium hydroxide. Anhydrous sodium perchlorate was prepared by crystallization from a saturated solution at a temperature above the transition temperature of 530°,[21] dried in a vacuum desiccator and found by a Karl Fischer titration, to contain about 0.045% water. The neutrality of the sodium perchlorate was shown by the fact that for a 1 *M* methanolic solution, the amount of base required to titrate to the brom thymol blue end-point and the amount of acid required for the brom phenol blue end point were both the same as the amounts required for pure methanol, within the experimental error.

To prepare the 1,1,1,3-tetranitro-2-phenylpropane, 13.6 g. of nitroform was added to a solution of 8.94 g. of β-nitrostyrene in methanol. Water was added to the cloud point and the mixture was kept at 40° for 4 hours. Upon cooling and filtering, 5.75 g. of white crystals was obtained and the mother liquors reheated to 40° for 4 more hours. A second cooling and filtration gave an additional 2.75 g. of product. Upon recrystallization from hexane, the combined crystals gave 7.39 g. (41%) of white needles, m.p. 87–88°.

Spectral Measurements.—By use of a Beckman model DU spectrophotometer, it was shown that the β-nitrostyrene has an absorption maximum at 3100 Å. and that the nitroform anion has one at 3500 Å. The absorption of nitroform and HA was small above 3000 Å. Beer's law plots gave straight lines and the extinction coefficients shown in Table IV.

TABLE IV

EXTINCTION COEFFICIENTS[a]

Species	ϵ_{3100}[b]	ϵ_{3500}[c]	ϵ_{3700}[c]
β-Nitrostyrene	16463	2922	687
Nitroform anion	2595	14847	7546
Nitroform	35	~0	~0

[a] ϵ for HA ~ 0 at 3100-3700 Å. [b] Slit 0.64 mm. [c] Slit 0.50 mm.

Ionization Constant of Nitroform.—The ionization constant of nitroform in methanol was determined by measurements of the concentration of the nitroform anion (from spectral data at 3500 Å.) in solutions with known formal concentrations of nitroform and in some instances hydrogen chloride and/or sodium perchlorate. The results obtained are listed in Table V.

TABLE V

IONIZATION CONSTANTS (K_N) OF NITROFORM IN METHANOL

Ionic strength	$K_N \times 10^4$ 25°	40°
0.5	17.6	
.3	11.8	
.2	9.41	9.39
.1	5.92	5.86
.04	3.61	
.002	1.30	
.000[a]	1.20[a]	

[a] Extrapolated.

Kinetic Studies with Pyridine Buffers.—In a typical run 0.002080 g. of HA was weighed into a 50-ml. low-actinic glass volumetric flask, and 45 ml. of methanolic pyridine-pyridine hydrochloride buffer and 5 ml. of 1.00 *M* methanolic sodium perchlorate, both at 25°, were added. The solution was shaken and a sample placed in a quartz cell in the 25 ± 0.1° thermostated cell compartment of the spectrophotometer. Optical density readings at 3700 Å. were made at various times and for the points between 10 and 75% reaction, first-order rate constants were calculated from the equation

$$k = \frac{2.303}{t} \log \frac{D_\infty}{D_\infty - D}$$

where D is the optical density at time t and D_∞ that at infinite time. Test experiments showed that in the buffers used nitroform is present entirely as the anion, within experimental error. Our observed values of D_∞ as well as calculations based on the equilibrium constant show that the reaction proceeds essentially to completion under the conditions used.

The results obtained are listed in Table VI. In the experiments said to be at 38°, the absolute temperature is correct within 0.3° and the temperature held within 0.1° for any given run.

Kinetic Studies in Methanolic Hydrogen Chloride.—Reaction solutions were made up by adding standard meth-

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(17) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(18) C. K. Ingold, ref. 2, Sec. 30a.

(19) A. K. Macbeth and W. B. Orr, *J. Chem. Soc.*, 534 (1932).

(20) A. I. Vogel, "Textbook of Practical Organic Chemistry," 2nd ed., Longmans, Green and Co., London, p. 168.

(21) E. Cornec and J. Dickely, *Bull. soc. chim. France*, [4] **41**, 1017 (1923).

TABLE VI

DECOMPOSITION OF HA IN A METHANOLIC PYRIDINE BUFFER AT 25°

[HA] = 1.385 × 10⁻⁴ *M*, [C₅H₅N] = [C₅H₅NH⁺] = 4.144 × 10⁻³ *M*, [NaClO₄] = 0.100 *M*

Time, sec.	Optical density^a	$\log \frac{D_\infty}{D_\infty - D}$	$10^5 k$, sec.$^{-1}$
3960	0.151	0.0614	3.57
4560	.173	.0715	3.62
12360	.411	.1931	3.60
13560	.441	.2111	3.58
14760	.468	.2281	3.57
15960	.496	.2465	3.55
16560	.510	.2560	3.57
		Av.	3.58 ± 0.02

[a] D_∞ = 1.150, the calculated value is 1.140.

anolic hydrogen chloride to weighed samples of HA and then adding enough 1.00 *M* sodium perchlorate to bring the ionic strength to 0.100. At given times samples were pipetted from the reaction flask in a 40 ± 0.1° bath into a spectrophotometer cell at 25° and the optical density at 3100 and 3500 Å. determined. From these measurements and the ionization constants of nitroform under these conditions, the concentrations of β-nitrostyrene and nitroform were calculated and substituted into the integrated form of the first-order rate equation. The reaction was relatively slow and was only followed to about 20% of completion since β-nitrostyrene was found to decompose in methanol at a rate sufficient to have produced significant errors if we had tried to follow the reaction much further. Calculations based on K_e show that the reaction should proceed to more than 99% completion under the conditions used in these experiments.

Kinetics of the Addition of Nitroform to β-Nitrostyrene and Determination of K_e.—To 1.0518 g. of β-nitrostyrene in a 50-ml. low-actinic volumetric flask were added 20 ml. of 1.0380 *M* nitroform, 5 ml. of 1.00 *M* sodium perchlorate and 25 ml. of methanol. The flask was shaken, placed in a thermostated bath at 40 ± 0.1°, and at measured times 5-ml. samples were transferred into 45 ml. of ~ 0.5 *M* methanolic hydrogen chloride, to quench the reaction. A 5-ml. aliquot of this solution was then diluted to 100 ml. with methanol to give a solution of which 5 ml. was removed and diluted to 50 ml. Optical density measurements were made at 3100 and 3500 Å. on this final solution which was 2000 times as dilute as the reaction mixture. From these measurements, the concentrations of reactants and products were calculated. The resultant data are listed in Table VII and plotted (open circles) in Fig. 2. Also plotted in Fig. 2 is a run made with $[HNF]_0$ = 0.0909, [NS] = 0.0713, [NaClO₄] = 0.000.

TABLE VII

ADDITION OF NITROFORM TO β-NITROSTYRENE IN METHANOL AT 40°

Time, hr.	Optical density 3100 Å.	Optical density 3500 Å.	[NS]^a
0.0	0.583	0.135	0.1402
2.5	.538	.113	.1340
4.5	.503	.119	.1208
21.5	.366	.081	.0884
24.5	.356	.076	.0860

[a] Initial value of $[HNF]_{formal}$ = 0.4152 *M*.

Runs used to determine the value of K_e were carried out similarly except that no sodium perchlorate was used, and in some cases HA was used as the reactant. The data obtained are plotted in Fig. 2.

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ATLANTA, GA.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Phenyl Migration during Decomposition of Peroxides in Alkylbenzenes[1a,b]

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The decomposition of peroxides in alkylbenzenes was studied. Decomposition of di-*t*-butyl peroxide in cumene and *t*-butylbenzene yielded, in addition to the products previously reported in the literature, *n*-propylbenzene in small yield and isobutylbenzene, respectively. *t*-Amylbenzene under similar conditions yielded 2-phenyl-3-methylbutane and 1-phenyl-2-methylbutane. Peroxides giving rise to more reactive free radicals, namely, benzoyl peroxide and acetyl peroxide, also caused similar isomerizations, but to a lesser extent. With the latter peroxides, reactions with the aromatic nucleus became more important than side-chain hydrogen abstraction. The decomposition of di-*t*-butyl peroxide in cumene at higher temperature is accompanied by side-chain methylation resulting in the formation of *t*-butylbenzene.

Recently[1,2] it was observed in this Laboratory that during the thermal reaction of alkylbenzenes with olefins 1,2-aryl migrations took place readily. In all the cases studied, the migration was that of a phenyl group to an adjacent terminal carbon atom. For example, during the thermal reaction of cumene with propylene, in addition to the normal side-chain alkylation products, the rearranged product 2-methyl-1-phenylpentane was also detected. This product was evidently formed by the migration of the phenyl group of 2-methyl-2-phenylpentane to the adjacent terminal carbon atom. The alternate type of migration, namely, to the adjacent non-terminal carbon atom, would have led to 2-methyl-3-phenylpentane. However, this product was not detected. In view of this it was of interest to see if the radical produced by the removal of a β-hydrogen atom of an alkylbenzene under less severe conditions will rearrange. Specifically, it was of interest to see what type of rearrangement, if any, will take place as a result of hydrogen abstraction from *t*-amylbenzene. With these ends in mind the decompositions of peroxides in isopropylbenzene, *t*-butylbenzene and *t*-amylbenzene were studied.

Several instances of 1,2-phenyl migration during free radical reactions are to be found in the literature. Among the most well-known of these are

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[1] (a) Paper III of the series, "Thermal Alkylation Reactions." For paper II, see H. Pines and C. N. Pillai, THIS JOURNAL, **81**, 3629 (1959). (b) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Fund.

[2] H. Pines and J. T. Arrigo, THIS JOURNAL, **79**, 4957 (1957).