The reaction orders were obtained from the t_{10} values corresponding to reactions in solutions 0.01 M (Table I) and 0.02 M in both reactants. In the latter concentrations the t_{10} values for bromodurene and chloromesitylene in nitromethane and for fluorodurene in acetic acid were found to be 8.6, 12.0 and 35.0 minutes, respectively.

The over-all acceleration of bromination in going from acetic acid to nitromethane solutions was obtained on multiplication of the acceleration observed with durene from acetic acid to mixed solvent solutions by the acceleration observed with a number of compounds from mixed solvent to nitromethane solutions. From the mean values of t_{10} reported in Table I, the former acceleration is given by the ratio 339/5.47, whereas the latter acceleration is given by the ratio 150/28.3 as obtained from fluoromesitylene and by any similar ratio obtained from other compounds, such as chloromesitylene, chlorodurene and bromodurene. For the over-all acceleration a mean value of 331 ± 5 was obtained.

Extent of Side-chain Bromination.—Dark bromination in a polar solvent of alkylated aromatic compounds is expected to occur at the ring carbon atoms. In order to ascertain this point we have carried out side-chain bromination tests for a number of the compounds examined in this work under conditions essentially similar to the kinetic experiments. In all cases we found that the extent of side-chain substitution is so small that it affects over-all rates but negligibly. A side-chain bromination test for mesitylene in acetic acid solution has been recently reported by Keefer, *et al.*[16] By adopting such a test for isodurene, the extent of side-chain reaction was found to be 0.33%. In the case of the brominations carried out in nitromethane solution, we have worked out the following modified procedure. A solution (20 ml.) approximately 0.1 M with respect to the aromatic compound and 0.05 M with respect to bromine, was allowed to stand in the dark for ten days. After withdrawing a 1-ml. sample for the determination of the unreacted bromine, to the remaining solution aqueous potassium iodide and sodium thiosulfate were successively added under vigorous shaking. After addition of ether, the mixture was transferred into a separatory funnel and the organic layer thoroughly washed with distilled water to eliminate all halide ions. Then the ether was removed and the remaining liquid was treated with an excess of alcoholic silver nitrate solution and the bromide ion thus set free was determined gravimetrically. The extent of the total bromination was 72 to 87% depending on the aromatic compound used. In the case of bromomesitylene, fluoromesitylene, chloroisodurene and iododurene the extent of side-chain bromination was found to be 1.3, 0.3, 0.57 and 0.31%, respectively.

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ROME, ITALY

[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

aci-Nitroalkanes. I. The Mechanism of the ter Meer Reaction[1]

BY M. FREDERICK HAWTHORNE

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The reaction of 1-chloronitroethane with nitrite ion to produce 1,1-dinitroethane (ter Meer reaction) has been found to proceed through the isomerization of the chloronitroethane to its *aci*-isomeride followed by a bond-making type of nucleophilic displacement of halogen by nitrite ion. This conclusion is based on the facts: (1) The reaction may be inhibited by the addition of excess strong base, (2) the reaction displays a first-order dependence on both nitrite ion and chloronitroethane at high nitrite ion concentrations and that under these conditions the rate-determining process is the nitrite ion (general base) catalyzed ionization of the chloronitroethane and (3) the substitution of deuterium for protium alpha to the chloro and nitro substituents produces a primary kinetic isotope effect of approximately 3.3 when the reactions are compared at high nitrite ion concentrations. It is suggested that the formation of *sym*-dialkyl dinitroethenes from 1-halonitroalkanes in basic solution and the solvolysis of 1-chloronitroethane proceed by similar mechanisms.

It is the purpose of this paper to prove that the *aci*-isomerides of 1-halo-1-nitroalkanes are reactive substrates in nucleophilic displacement reactions and that these displacement reactions furnish an explanation for certain syntheses and kinetic measurements which have been reported heretofore. As a model reaction, the synthesis of 1,1-dinitroethane from 1-chloronitroethane and nitrite ion in basic solution[2] has been chosen for kinetic study using the model compound 1-chloronitroethane in 50% (volume) aqueous ethanol at 29.8°.

Results

In order to examine the kinetics of the ter Meer reaction using 1-chloronitroethane an analytical method for the determination of 1,1-dinitroethane was required as well as a method for the rapid quenching of the reaction mixtures. Spectrophotometric examination of solutions of 1,1-dinitroethane in approximately 0.10 N sodium hydroxide (in 50% by volume aqueous ethanol) proved that the 1,1-dinitroethane anion was produced quantitatively, obeyed Beer's law at the 380 mμ maximum (ϵ 1.6 × 10^4) and was stable under these conditions for reasonable periods of time.

Similarly, it was found that the anion of 1-chloronitroethane was produced quantitatively and at an immeasurably rapid rate when a few milligrams of the chloronitroalkane was added to a large excess of this basic solution. The ultraviolet absorption spectrum of this anion exhibited a well defined peak at 237 mμ (ϵ = 1.00 × 10^4) which remained unchanged for at least one hour. Table I records the stability of 1-chloronitroethane dissolved in an excess of dilute ethanolic base at 30° in terms of the amount of chloride ion liberated by hydrolysis.

TABLE I

THE EXTENT OF DECOMPOSITION OF 1-CHLORONITROETHANE IN THE PRESENCE OF EXCESS HYDROXIDE ION IN 50% (VOLUME) AQUEOUS ETHANOL AT 30°

Initial concentration, moles/l. 1-Chloro-1-nitroethane	Initial concentration, moles/l. Hydroxide ion	Elapsed time, hours	Final chloride ion concn., mole/liter	Reaction, %
0.0749	0.0949	17.0	0.0045	6.0
.0402	.0949	16.5	.0021	5.2

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] E. ter Meer, *Ann.*, **181**, 4 (1876).

It is readily seen from these results that an aliquot of a reaction mixture containing 1,1-dinitroethane and 1-chloronitroethane could be quantitatively analyzed for 1,1-dinitroethane spectrophotometrically and the reaction of 1-chloronitroethane quenched by delivering the aliquot to a large excess of a dilute aqueous ethanolic sodium hydroxide solution.

Kinetic measurements were carried out at 29.80 ± 0.05° in 50% (by volume) aqueous ethanol at an initial 1-chloronitroethane concentration of 1.14 $\times 10^{-2}$ *M* and in the presence of a large excess of sodium nitrite. Aliquots were taken periodically, quenched with 0.10 *N* sodium hydroxide and the optical density determined at 380 mμ. Since nitrite ion was found to have a molar extinction coefficient of 16 at this wave length, all experimental points were corrected for the appropriate amount of nitrite ion absorption. At least ten experimental points were taken in each run and the reaction followed to 80% conversion in every case. 1,1-Dinitroethane was shown to be the only important product of these reactions by comparison of the ultraviolet absorption spectrum of each reaction mixture at greater than 90% reaction with that of authentic 1,1-dinitroethane anion. Furthermore, the high degree of reproducibility (±5%) of the second-order rate constant throughout each kinetic experiment and the fact that these constants were calculated on the assumption of complete conversion of 1-chloronitroethane to 1,1-dinitroethane indicate that no other kinetically important reaction has occurred.

Indeed, a reaction was carried out to 37% conversion (measured spectrophotometrically) using conditions similar to those employed in the rate experiments and 47% of the yellow material absorbing at 380 mμ was isolated as the ammonium salt of 1,1-dinitroethane (see Experimental). Table II presents a set of experimental observations for one run and Table III contains a summary of all rate determinations using 1-chloronitroethane.

TABLE II

THE KINETICS OF THE REACTION OF 1.14 $\times 10^{-2}$ *M* 1-CHLORONITROETHANE WITH 0.40 *M* SODIUM NITRITE AT 29.80 ± 0.05° IN 50% BY VOLUME ETHANOL

Time, min.	Optical density (380 mμ)	Pseudo 1st order constant, min.$^{-1}$ $\times 10_3$
0.0	0.00	
15.5	.20	7.42
24.1	.29	7.06
37.8	.39	6.35
45.9	.49	6.79
60.4	.62	6.82
72.6	.72	6.88
87.2	.79	6.47
114.4	.98	6.71
145.2	1.15	6.80
165.8	1.24	6.81
200.2	1.36	6.78
250.7	1.49	6.70
∞	1.83	Av. = 6.80 $\times 10^{-3}$

Second-order constant = 1.70 $\times 10^{-2}$ (l./mole-min.)

Inspection of Table III shows that although the concentration of nitrite ion was varied fourfold the second-order rate constant did not vary beyond experimental error.

TABLE III

THE RATES OF REACTION OF 1.14 $\times 10^{-2}$ *M* 1-CHLORONITROETHANE WITH EXCESS NITRITE ION AT 29.80 ± 0.05° IN 50% BY VOLUME ETHANOL

Concn. nitrite ion, mole/l.	Average 2nd order rate constant, l./mole-min. $\times 10^2$
0.20	1.64
.40	1.70
.80	1.61

The fact that the reaction of 1-chloronitroethane with large excesses of nitrite ion is first-order in both 1-chloronitroethane and nitrite ion suggests two mechanistic possibilities: (1) the direct displacement of chloride ion from 1-chloronitroethane by nitrite ion or (2) the nitrite ion catalyzed rate-determining isomerization of 1-chloronitroethane to its more reactive *aci*-isomeride.

It is possible to choose the correct mechanism of the reaction by studying the kinetics of the formation of 1,1-dinitroethane from 1-deutero-1-chloronitroethane and nitrite ion. If the rate-determining process of the kinetic experiments is the nitrite ion catalyzed ionization of the nitroalkane the rate of formation of 1,1-dinitroethane from the deuterated substrate should be much less than that of the protium analog.[3] Accordingly, 1-deutero-1-chloronitroethane was prepared in 55% yield by the neutralization of the 1-chloronitroethane anion in 98% deuterium oxide with acetic acid. If a statistical distribution of deuterium is assumed, the material obtained should contain approximately 93% of the deuterated nitroalkane. The nitroalkane obtained gave acceptable analyses for nitrogen and chlorine, was converted quantitatively to the 1-chloronitroethane anion in the manner described above, appeared to be pure by vapor phase chromatography and had physical constants close to those of the protium analog. The infrared spectrum of this material was compared to that of pure undeuterated material and several distinct differences were noted. The C–H stretching band at 3.37 μ decreased in intensity on deuteration and new bands appeared at 4.44, 4.53, 10.83 and 12.05 μ and a band was lost at 7.75 μ.

Table IV presents the data obtained in a single rate experiment using 1-deutero-1-chloronitroethane as substrate and the experimental conditions described above for the protium analog. Table V is a summary of all the rate data obtained in this manner.

These data clearly show that the second-order reaction of 1-deutero-1-chloronitroethane with nitrite ion is approximately one-third as rapid as that of the protium compound under identical conditions. The fact that the second-order rate constant obtained in each rate experiment remained constant up to at least 80% reaction and that the final conversion to 1,1-dinitroethane was quantitative within experimental error lend considerable support to the chemical and isotopic purity of the deuterated chloronitroalkane.

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[3] See C. L. Wilson, *Trans. Faraday Soc.*, **34**, 184 (1935), for a collection of references pertaining to the primary isotope effect in deuterated nitroalkane ionization.

TABLE IV

THE KINETICS OF THE REACTION OF 1.14 × 10^{-2} *M* 1-DEUTERO-1-CHLORONITROETHANE WITH 0.40 *M* SODIUM NITRITE AT 29.80 ± 0.05° IN 50% BY VOLUME ETHANOL

Time, min.	Optical density (380 mμ)	Pseudo 1st order rate constant, $\text{min.}^{-1} \times 10^{-3}$
0.0	0.00	
60.6	.20	1.98
94.4	.33	2.10
124.7	.41	2.02
165.0	.54	2.12
205.5	.66	2.18
246.4	.75	2.14
305.8	.86	2.08
397.4	1.00	1.98
460.3	1.11	2.05
605.3	1.27	1.97
740.1	1.42	2.02
∞	1.83	

Av. = 2.03×10^{-3}

Second-order constant = 5.08×10^{-3} l./mole-min.

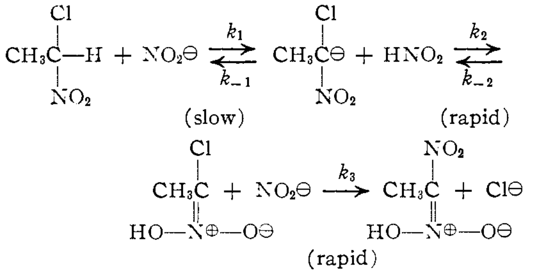
TABLE V

THE RATES OF REACTION OF 1.14 × 10^{-2} *M* 1-DEUTERO-1-CHLORONITROETHANE WITH EXCESS NITRITE ION AT 29.80 ± 0.05° IN 50% BY VOLUME ETHANOL

Concentration nitrite ion, mole/l.	Average 2nd order rate constant, l./mole-min. × 10^3
0.20	5.52
.40	4.89
.40	5.08
.80	4.85

Discussion

The occurrence of a primary kinetic isotope effect of 3.3 unequivocally proves that the rate-controlling step of the ter Meer reaction is the slow nitrite ion catalyzed ionization of the 1-chloronitroalkane when the reaction is conducted in the presence of high concentrations of nitrite ion. Furthermore, it shows that the substrate which is rapidly attacked by nitrite ion is either the carbanion itself or a species which may be produced from it at a rate greater than that with which the anion returns to hydrocarbon. Since the anion of 1-chloronitroethane is relatively stable in the presence of 0.1 *N* hydroxide ion and hydroxide ion is an extremely powerful nucleophile, it follows that the substrate which reacts with nitrite ion is not the anion of 1-chloronitroethane. However, the 1-chloronitroethane anion is in rapid equilibrium with *aci*-1-chloronitroethane and this later species must be the reactive substrate.



$$CH_3CCl(NO_2)H + NO_2^{\ominus} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3CCl(NO_2)^{\ominus} + HNO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \quad \text{(slow)} \quad \text{(rapid)}$$

$$CH_3CCl{=}N^{\oplus}(OH)O^{\ominus} + NO_2^{\ominus} \xrightarrow{k_3} CH_3C(NO_2){=}N^{\oplus}(OH)O^{\ominus} + Cl^{\ominus} \quad \text{(rapid)} \qquad (1)$$

This rationale is formalized as

$$d[CH_3CH(NO_2)_2]/dt = k_3[\text{aci}][NO_2^{\ominus}] \qquad (2)$$

where

$$[\text{aci}] = [CH_3CHClNO_2] \times \frac{k_2[HNO_2]k_1[NO_2^{\ominus}]}{[NO_2^{\ominus}](k_{-1} + k_2)[HNO_2] + k_{-2}[NO_2^{\ominus}]k_{-1}[HNO_2]} \qquad (3)$$

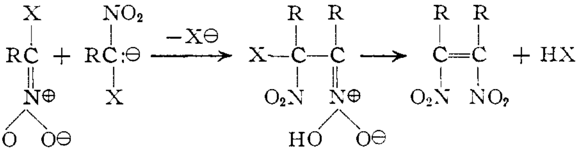
and if k_1 and $k_{-1} << k_2$, k_{-2} and k_3

$$d[CH_3CH(NO_2)_2]/dt = [CH_3CHClNO_2]k_1[NO_2^{\ominus}] \qquad (4)$$

Although the reaction medium employed in the kinetic experiments contained 50% of water by volume and hydroxide ion was produced by the hydrolysis of nitrite ion, no significant hydroxide ion or solvent terms appeared in the kinetic analysis.[4] This is probably due to the high concentrations of nitrite ion employed and the magnitude of the error inherent in the rate experiments.

The rapid displacement of chloride ion from *aci*-1-chloronitroethane by nitrite ion is an interesting example of nucleophilic attack on a carbon atom which is probably closely akin to the carbonyl carbon atom of acyl halides. The fact that N- to the exclusion of O-alkylation is observed agrees well with the recent generalizations of Kornblum, *et al.*,[5] and points up the fact that nucleophilic attack occurs on an unsaturated carbon atom in a bond-making type transition state.

Two other examples of the apparent nucleophilic displacement of halide ion from *aci*-1-halonitroalkanes are to be found in the literature. The synthesis of *sym*-dialkyl dinitroethenes in 30–40% yield by treatment of excess 1-halo-1-nitroalkanes with aqueous base[6,7] may be interpreted as the nucleophilic attack of the 1-halo-1-nitroalkane anion upon the *aci*-1-halo-1-nitroalkane followed by elimination of hydrogen halide. The "ambident ion" principle of Kornblum, *et al.*,[5] is again invoked to explain the occurrence of C-alkylation.



$$RCX{=}N^{\oplus}(OH)O^{\ominus} + RC(NO_2)X^{\ominus} \xrightarrow{-X^{\ominus}} X{-}CR(NO_2){-}CR{=}N^{\oplus}(OH)O^{\ominus} \longrightarrow RC(NO_2){=}CR(NO_2) + HX$$

Secondly, the observations of Pearson and Dillon[8] may be similarly interpreted as involving *aci*-1-chloronitroethane. These authors reported that 1-chloro-1-nitroethane hydrolyzed in water at 34.9° to produce chloride ion and unidentified products at a rate described by equation 5.

$$d[Cl^{\ominus}]/dt = 4.8 \times 10^{-5}\ \text{min.}^{-1}\ [CH_3CHClNO_2] \qquad (5)$$

Furthermore, they reported that this hydrolysis reaction did not occur in the presence of bromine but instead bromine was consumed at the same temperature by a rate described by equation 6.

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[4] Assuming the dissociation of water to be 1×10^{-14} in 50%, by volume, aqueous ethanol and the pK_A of nitrous acid to be about 4, the concentration of hydroxide ion, in the reaction media is given by $[OH^{\ominus}] = 10^{-5}[NO_2^{\ominus}]^{1/2}$.

[5] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955).

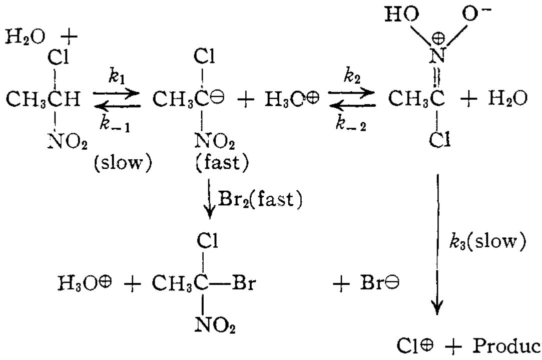
[6] E. M. Nygaard and T. T. Noland, U. S. Patent 2,396,282 (1946)

[7] A personal communication from L. B. Clapp states that this reaction may be carried out by the partial neutralization of the anion of a 1-halo-1-nitroalkane with strong mineral acid. Reaction ensues as solution approaches *p*H 9.

[8] R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

$$-d[Br_2]/dt = 1 \times 10^{-4}\ \text{min.}^{-1}\ [CH_3CHClNO_2] \quad (6)$$

This rate of bromine consumption was identified with the rate of ionization of the chloronitroalkane since the anion of the chloronitroalkane should react immeasurably fast with bromine. Comparison of the first-order rate constants of equations 5 and 6 shows that bromine consumption is exactly twice as rapid as the hydrolytic production of chloride ion. All these observations may be explained on the basis of the reaction sequence (7) in which water nucleophilically attacks the carbon atom of *aci*-chloronitroethane at a rate equal to that with which hydronium ion donates a proton to the carbanion to produce starting material. (Since k_3k_{-1} is undoubtedly small compared to $k_{-1}k_{-2}$ and k_3k_2, the expressions corresponding to equations 2 and 3 give $k_3 = k_{-1}k_{-2}/k_2$.)



(7)

Experimental

Materials.—Aqueous ethanol (50% by volume) was prepared by mixing equal volumes of U. S. P. absolute ethanol and distilled water at 25°.

Sodium nitrite and sodium hydroxide were C.P. reagents and used without further purification.

1-Chloronitroethane was obtained from the Commercial Solvents Corp. and purified with 50% recovery as described by Pearson and Dillon.[8] The purified product was fractionated using a 20-plate Nestor spinning-band fractionating column at atmospheric pressure. A middle portion of the distillate was taken which boiled at 125° (755 mm.), n^{25}D 1.4230.[9] A portion of this material was chromatographed on a eight-foot vapor phase chromatographic column composed of 70% infusorial earth and 30% Dow-Corning 550 Fluid at 100°, atmospheric pressure and with helium carrier gas. Only one peak was obtained. A control experiment using crude 1-chloronitroethane gave two peaks; a small peak which was eluted first followed by a large 1-chloronitroethane peak.

The compound was further characterized by N and Cl analyses. Calcd. for $C_6H_4NO_2Cl$: N, 12.79; Cl, 32.38. Found: N, 12.45; Cl, 31.92.

The infrared spectrum of this material showed no carbonyl bands and no 10.75 μ band characteristic of 1,1-dichloronitroethane when run neat in a 0.1-mm. NaCl cell using a Perkin–Elmer model 21 spectrophotometer.

1-Deutero-1-chloronitroethane was prepared by dissolving 10.0 g. (0.091 mole) of purified 1-chloronitroethane in 25 ml. (1.52 moles) of 98% deuterium oxide containing 5.0 g. (0.125 mole) of sodium hydroxide and extracting the resulting solution with pure ether. The aqueous solution was cooled and 75 ml. (3.96 moles) of deuterium oxide added followed by 0.50 g. (0.007 mole) of hydroxylamine hydrochloride. Six grams (0.10 mole) of glacial acetic acid was then added rapidly. After 30 minutes the solution was extracted with three 100-ml. portions of pure ether, the ether layer washed well with water and dried over magnesium sulfate. The ethereal solution of product was concentrated under a 20-plate Nestor spinning-band column and the residual oil fractionated at atmospheric pressure. The center third of the distillate (1.80 g.) was collected separately, b.p. 125° (755 mm.), n^{25}D 1.4228. The total distillate weighed 5.50 g. (55% recovery), b.p. 125° (755 mm.). The first and third cuts had n^{25}D 1.4226 and 1.4230, respectively.

A vapor phase chromatogram obtained as described above using the center cut gave only one peak and the material analyzed as follows: Calcd. for $C_2H_3DNO_2Cl$: N, 12.68; Cl, 32.09. Found: N, 12.32; Cl, 32.35.

The infrared spectrum of the center cut showed no carbonyl bands and no 10.75 μ band which is characteristic of 1,1-dichloronitroethane. Comparison of the spectrum of this material with that of the protium compound showed that deuteration produced new bands at 4.44, 10.83 and 12.05 μ and a band was lost at 7.75 μ. The spectrum was run neat in a 0.1-mm. NaCl cell using a Perkin–Elmer model 21 spectrophotometer.

1,1-Dinitroethane was supplied by the Commercial Solvents Corp. and cautiously redistilled before use, b.p. 50° (5 mm.), n^{25}D 1.4321.

Spectrophotometric Measurements.—All ultraviolet and visible spectrophotometric measurements were carried out with a Beckman model DK-1 recording spectrophotometer at room temperature and in 50% by volume aqueous ethanol solvent.

1-Chloronitroethane and 1-deutero-1-chloronitroethane prepared and purified as described above were examined in 0.1 *N* sodium hydroxide solution at concentrations of 1.50, 1.00 and 0.50 × 10^{-4} *M*. In each case and at each concentration the spectra were superimposable after correction for concentration differences and had a maximum at 237 mμ with a molar extinction coefficient of 1.00 × 10^4. The spectra were all examined immediately after mixing the proper volumes of a freshly prepared 50% by volume aqueous ethanol stock solution of chloronitroalkane with the proper volume of 0.1 *N* sodium hydroxide solution. The spectra remained unchanged for at least one hour.

1,1-Dinitroethane described above was carefully weighed into several 10-ml. volumetric flasks and made up to volume with 0.1 *N* sodium hydroxide solution in 50% by volume ethanol. The solution in each flask was carefully diluted to a predetermined volume by transfer of a small aliquot to a larger volume of 0.1 *N* sodium hydroxide in the same solvent. The concentrations of these final solutions varied from 1.15 to 0.4 × 10^{-4} *M*. In each case the complete spectrum was scanned from 600 to 220 mμ and the spectra were superimposable after correction for concentration differences. The dilute solutions remained unchanged for at least 12 hours and exhibited a molar extinction coefficient of 1.60 × 10^4 at the 380 mμ maximum.

Kinetic Measurements.—All kinetic measurements were made under pseudo first-order reaction conditions using freshly prepared solutions of 97% sodium nitrite in 50% by volume aqueous ethanol at 29.80 ± 0.05°. Each solution was prepared by carefully weighing the proper amount of sodium nitrite into a 250-ml. volumetric flask and making the solution up to the mark at room temperature. Twenty-five milliliters of each sodium nitrite solution was placed in a 50-ml. volumetric flask and allowed to stand in the thermostat for one-half hour before beginning the run. The reaction was initiated by the addition of 3.13 × 10^{-2} g. (2.85 × 10^{-4} mole making a 1.14 × 10^{-2} *M* solution) of 1-chloronitroethane or its deuterated analog (center cut described above) from an accurately calibrated micropipet. The solvent cell of the spectrophotometer was filled with a solution of 0.100 ml. of the sodium nitrite used diluted to 10.00 ml. with 0.1 *N* sodium hydroxide in 50% aqueous ethanol in order to cancel the absorption of the reaction mixture due to nitrite ion (ϵ 16 at 380 mμ). At various time intervals a 0.100-ml. aliquot of the reaction solution was withdrawn and rapidly delivered to 5–6 ml. of 0.1 *N* sodium hydroxide solution at room temperature. This treatment effectively stops the reaction both by dilution and conversion of the chloronitroethane to its sodium salt. The time of mixing was taken as the point time. The volumetric flask was then filled to the mark with the same alkaline solution and its optical density determined at 380 mμ. Approximately twelve points were taken in each run and the reaction followed until the rate became inconveniently low (usually near 80% reaction). Infinity values of the optical density were determined 12 hours after the last point was taken and were equal to the value calculated (1.83 ± 0.05). The complete spectrum of these solutions was determined from 600 to 240

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[9] Pearson and Dillon (ref. 8) report n^{25}D 1.4235.

mμ and was identical with that of 1,1-dinitroethane in the same solvent mixture. In every run the calculated second-order constant remained constant up at least 80% reaction when calculated on the basis of complete conversion to 1,1-dinitroethane at infinite time. Exactly the same procedure was used for the deuterated substrate, the 1% difference in molecular weight and the small density difference being neglected. The data obtained in all runs was treated using the first-order integrated equation and the second-order constant evaluated from a knowledge of nitrite ion concentration.

The data given in Table I for the extent of decomposition of 1-chloronitroethane at 30° in the presence of excess 0.1 *N* sodium hydroxide in 50% by volume aqueous ethanol were obtained in the following manner: The proper amount of 1-chloronitroethane was weighed into a 100-ml. volumetric flask and the flask filled to the mark with standard 0.1 *N* sodium hydroxide in 50% ethanol. The flask was immersed in a 30° thermostat and a 5-ml. aliquot of reaction mixture transferred to 25 ml. of a 5% sodium bicarbonate solution after the required time interval had elapsed. A few drops of gum arabic solution was added along with 1 ml. of a 1% potassium chromate solution and the solution titrated to a permanent pink with standard 0.10 *N* silver nitrate solution.

Isolation of 1,1-Dinitroethane as Ammonium Salt.—Ten grams of potassium nitrite (0.117 mole) was dissolved in 75 ml. of water and a solution of 0.313 g. (2.85×10^{-3} mole) of the 1-chloronitroethane described above dissolved in 25 ml. of ethanol was added. The reaction mixture was allowed to stand at room temperature for one hour. An aliquot of this reaction mixture (0.100 ml.) was then taken, diluted to 10 ml. as described above and its absorption spectrum determined. The single peak at 380 mμ gave an optical density of 1.72 after correction for nitrite ion absorption and indicated that the reaction mixture contained 1.06×10^{-3} mole of 1,1-dinitroethane (37% conversion of 1-chloronitroethane to 1,1-dinitroethane).

A mixture of 15.0 g. (0.216 mole) of hydroxylamine hydrochloride, 25 ml. of concentrated hydrochloric acid and 75 ml. of ether was placed in a 500-ml. flask bearing a reflux condenser, stirrer and dropping funnel and the flask cooled in an ice-bath. The dilute 1,1-dinitroethane solution described above was added slowly from the dropping funnel with vigorous stirring during the course of one-half hour. The resulting colorless mixture was saturated with sodium chloride and the ether layer separated and dried over magnesium sulfate. A saturated solution of ammonia in dry ether was added dropwise to the dry ether solution until ammonium chloride ceased to be precipitated and the yellow color of the ammonium salt of 1,1-dinitroethane began to appear. The solution was then filtered, concentrated to 10 ml. under reduced pressure and extracted with dilute ammonium hydroxide until the aqueous layer was no longer colored. The combined aqueous extracts were cautiously acidified with concentrated hydrochloric acid in the presence of ice and 50 ml. of ether and the ether layer separated, washed three times with water (aqueous layer became light yellow in color on last water wash), dried over magnesium sulfate and evaporated to 5 ml. under reduced pressure; 0.2 ml. of alcohol was added followed by 30 ml. of saturated ammoniacal ether. The precipitated yellow solid was collected on a filter and washed with ether. After air-drying it was found to weigh 65 mg. (4.7×10^{-4} mole) giving a 47% recovery of 1,1-dinitroethane.

The yellow solid sublimed at 127–128°,[10] had an infrared absorption spectrum identical with that of the authentic ammonium salt of 1,1-dinitroethane in a Nujol mull and gave an absorption peak at 380 mμ in dilute basic solution ($\epsilon = 1.6 \times 10^4$ calcd. on the basis of ammonium salt). The material was further characterized by elemental analysis. Calcd. for $C_2H_7N_3O_4$: N, 30.29; C, 17.46; H, 5.39. Found: N, 30.65; C, 17.52; H, 5.15.

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[10] J. S. Belew, C. E. Grabiel and L. B. Clapp, This Journal, **77**, 1110 (1955), report m.p. 90–93° dec. for the ammonium salt of 1,1-dinitroethane. An authentic sample prepared as described above did not melt but sublimed at 128–130° without apparent decomposition.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Nitroalkanes from Conjugated Nitroalkenes by Reduction with Complex Hydrides[1]

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Sodium trimethoxyborohydride, lithium borohydride, sodium borohydride and lithium aluminum hydride are satisfactory reducing agents for converting conjugated nitroalkenes to their corresponding nitroalkanes. The reduction reactions are accompanied by consecutive processes in which the initial reduction products add to the parent nitroölefins to give salts of the corresponding 1,3-dinitroalkanes and related polynitroalkanes of higher molecular weights. The unconjugated nitrocycloalkene, 1-(nitromethyl)-cyclopentene, is not reduced by excess sodium trimethoxyborohydride, even under isomerizing conditions. Excellent procedures have been developed for reducing D-*arabo*-tetraacetoxy-1-nitro-1-hexene with lithium borohydride or sodium borohydride to 1-nitro-1,2-dideoxy-D-*arabo*-hexitol tetraacetate.

An attractive route for synthesis of primary and secondary nitroalkanes involves reduction of the carbon–carbon double bonds of conjugated nitroolefins.[3] Catalytic hydrogenation of conjugated[4a–e] and unconjugated[4f] nitroölefins to nitroalkanes has been effected successfully; as yet, however, this reaction is unsatisfactory as a general method for preparing saturated nitro compounds. It has been reported that reverse addition of lithium aluminum hydride to 2-nitro-1-phenyl-1-propene[5a] and to conjugated polyfluoroalkylnitroalkenes[5b] results in formation of the corresponding nitroalkanes[5c]; at slightly higher temperatures and with different ratios of reagents, 2-nitro-1-phenyl-1-propene reacts with lithium aluminum hydride to give phenylacetone oxime, N-(β-phenylisopropyl)-hydroxylamine and β-phenylisopropylamine.[5a] Since borohydrides are generally inert to nitro groups[6a–f] and

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[2] This research has been abstracted principally from a dissertation submitted by Dean E. Ley to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, 1954.

[3] General methods of synthesis of conjugated nitroalkenes are summarized by (a) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 373 (1943), and (b) N. Levy and J. D. Rose, *Quart. Revs.*, **1**, 358 (1947).

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[5] (a) R. T. Gilsdorf and F. F. Nord, This Journal, **74**, 1837 (1952); (b) D. J. Cook, O. R. Pierce and E. T. McBee, *ibid.*, **76**, 83 (1954); (c) A. Dornow and W. Bartoch, *Ber.*, **87**, 633 (1954).

[6] (a) S. W. Chaikin and W. G. Brown, This Journal, **71**, 123 (1949); (b) R. F. Nystrom, S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 3245 (1949); (c) H. Shechter, D. E. Ley and L. Zeldin, *ibid.*, **74**, 3664 (1952); (d) H. C. Brown and E. J. Mead, *ibid.*, **75**, 6263 (1953); (e) D. C. Iffland and G. X. Criner, *ibid.*, **75**, 4047 (1953); (f) D. C. Iffland and Teh-Fu Yen, *ibid.*, **76**, 4083 (1954).