values calculated on the basis of complete conversion of nitroalkane to anion and complete reaction of the resulting *aci*-nitro tautomer. Acid concentrations present in each run were calculated on the basis of negligible ionization of the *aci*-nitroalkane and by the relationship

$$[H^+] = \frac{N(\text{ml. } N \text{ normal acid used}) - 2.00\ (N \text{ of base used})}{52.0}$$

In each run an acceptable first-order constant was obtained from log (optical density) *vs.* time plots. Figures 1 and 2 present the data obtained from one nitrocyclohexane run and from all runs with all nitroalkanes, respectively. Table I summarizes all second-order rate constants.

Spectrophotometric Measurements.—The ultraviolet absorption spectra of the nitroalkane anions recorded in Table II were determined in 80% methanol using a model DK-1 Beckman spectrophotometer and 1-cm. stoppered silica absorption cells. The nitroalkane anion solutions were prepared under nitrogen as described above and diluted with 50 ml. of solvent at room temperature in the reactor. Aliquots of these solutions were further diluted and immediately examined. Since the density of each nitroalkane examined was within a few per cent. of unity, the concentrations of nitroalkanes employed were calculated on the assumption that the 0.003 ml. of nitroalkane introduced was equal to 3 mg. of material. For this reason the extinction coefficients may be accurate only to ±5%.

Reaction products were analyzed for regenerated nitroalkane by making a run as described above and withdrawing no aliquots. The reaction mixture was then warmed to room temperature, and 5 ml. of 19 N (saturated) sodium hydroxide solution was added under nitrogen. After 1 to 2 hr. the spectrum of the basic reaction mixture was scanned using suitably diluted 19 N sodium hydroxide in the solvent cell. Only nitrocyclobutane showed absorption in the 230 mμ region. In two such experiments with this compound, the concentration of nitroalkane present in the basic solution before acidification was such as to give an optical density reading at 234 mμ of 0.91 after suitable dilution. After the Nef reaction had been carried out, the optical density observed at 232–234 mμ was 0.16 when concentrations were normalized to that of the original nitroalkane anion solution. About one-sixth of the nitrocyclobutane either survived the Nef reaction or the reaction produced a small amount of strongly absorbing impurity.

Ketone Isolation Procedure.—One-half gram samples of each nitroalkane were dissolved in 4.0 ml. of 2.5 N sodium hydroxide in 80% methanol in the reactor under nitrogen and at room temperature. After 0.5 hr., 50 ml. of 80% methanol was added and the solution cooled to 0° for 0.5 hr. Exactly 3.0 ml. of 12 N hydrochloric acid was added and the solution was stirred for 0.5 hr. In every case examined, acidification led to the immediate formation of a blue color. In each case, except those of 1-cyclopropylnitroethane and dicyclopropylnitromethane, this blue color rapidly disappeared. In the two abnormal cases the blue color persisted and finally disappeared as pseudonitrole separated from solution. Filtration of these solutions afforded about 5–10 mg. of unstable white solid which turned blue on solution in warm methylene chloride. A control experiment showed that 1-nitrosonitrocyclohexane was stable under these reaction conditions and indicates that pseudonitroles would have been isolated if they had been produced in other cases.

In every case the reaction mixture was placed on the steam-bath and warmed to 60°. At this point a slurry of 1 g. of 2,4-dinitrophenylhydrazine in 100 ml. of 6 N hydrochloric acid was added and the solution stirred and heated for 20 minutes, cooled to room temperature and filtered. The crude crystalline derivatives were washed with warm water, dried, weighed and melting points determined. Table III summarizes the yield data.

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

aci-Nitroalkanes. III. The Solvolysis of α-Chloronitrosocycloalkanes in the Presence of Electrophilic Silver Ion

BY M. FREDERICK HAWTHORNE AND R. DONALD STRAHM

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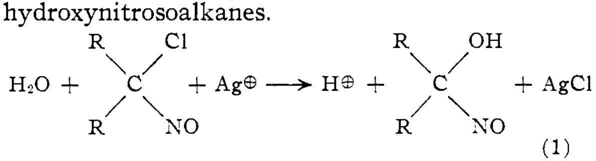
1-Chloronitrosocyclohexane and 1-chloronitrosocyclopentane are rapidly converted to cyclohexanone and cyclopentanone, respectively, in essentially quantitative yields when treated with silver perchlorate in 20:30:50 (by volume) ethanol: water:acetonitrile at 50.0°. The rates of these reactions were determined under the above conditions by titration of liberated hydrogen ion. The rate equation in each case is of the form $d[H^+]/dt = k[Ag^+]$[chloronitrosocycloalkane] with the second-order rate constant, k, equal to 2.0 and 5.0×10^{-2} l. mole^{-1} min.$^{-1}$ for 1-chloronitrosocyclohexane and 1-chloronitrosocyclopentane, respectively. No hydroxylamine, nitrogen, nitric oxide or nitrogen dioxide was produced and nitrous oxide was identified by gas chromatography. Silver chloride is produced in quantitative yield. It is suggested that these transformations probably proceed *via* the α-hydroxynitrosocycloalkanes which are in turn produced by the nucleophilic attack of water upon the α-carbon atom. This proposed path is in accord with recent proposals concerning the mechanism of the Nef reaction.

Because of our previous interest in the mechanism of the Nef reaction[1] and the probable relationship of the chemistry of α-hydroxynitrosoalkanes to that reaction, it was of interest to seek a more direct route to such materials and to determine their mode of decomposition in acidic aqueous media.

Piloty and Stock[2] long ago reported the synthesis of 2-nitro-2-nitrosopropane by the reaction of silver nitrite with 2-bromo-2-nitrosopropane in ethereal solution. This silver ion assisted displacement of bromide ion by nitrite ion probably proceeded by way of a concerted termolecular displacement reaction such as those recently characterized by Kornblum and Hardies[3] and by Hammond and Hawthorne.[4] It thus appeared probable that the similar treatment of 1-chloronitrosoalkanes with silver ion in the presence of water and in the absence of nucleophilic anions might yield α-hydroxynitrosoalkanes.



$$H_2O + R_2C(Cl)NO + Ag^{\oplus} \longrightarrow H^{\oplus} + R_2C(OH)NO + AgCl \quad (1)$$

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[1] M. F. Hawthorne, THIS JOURNAL, **79**, 2510 (1957).

[2] O. Piloty and A. Stock, *Ber.*, **35**, 3093 (1902).

[3] N. Kornblum and D. E. Hardies, Abstracts of the 130th Meeting of the American Chemical Society, September 16 to 21, 1956, Atlantic City, N. J., p. 2-O.

[4] G. S. Hammond and M. F. Hawthorne, Abstracts of the 126th Meeting of the American Chemical Society, New York, N. Y., September 12 to 17, 1954, p. 41-O.

Two reactions of this type have been studied from the viewpoint of reaction kinetics and product analysis.

Results

In order to test this hypothesis 1-chloronitrosocyclopentane and 1-chloronitrosocyclohexane were prepared[5] as recently described. Both materials could be stored in the dark at Dry Ice temperatures for long periods of time without decomposition. Preliminary solubility measurements indicated that these materials would dissolve in quantity in aqueous solvent systems only if this solvent contained ethanol. For this reason a ternary solvent system prepared from 2 volumes of ethanol, 3 volumes of water and 5 volumes of acetonitrile was utilized in the kinetic and product experiments.

The kinetics of the reaction of each of the 1-chloronitrosocycloalkanes with silver perchlorate was determined in the dark at 50.0° by titration of the hydrogen ion produced during each run. In every case the kinetics were of the form (2) and each kinetic experiment was carried to about 50% reaction. Initial silver perchlorate concentrations were varied four-fold (*ca.* 0.1 to 0.4 *M*) in each case while the initial 1-chloronitrosoalkane concentration was always near 0.2 *M*. Control experiments based on the spectrophotometric determination of the 1-chloronitrosoalkanes in the 620 mμ region proved that these materials were thermally and photochemically stable under the conditions of the kinetic experiments. Figure 1 gives a typical second-order plot obtained for both the cyclohexane and cyclopentane derivatives at the same initial concentration of reactants, and Table I records a summary of all the rate data obtained.

$$d[H^{\oplus}]/dt = k_2\,[Ag^{\oplus}][\text{1-chloronitrosocycloalkane}] \quad (2)$$

TABLE I

RATES OF SILVER ION ASSISTED SOLVOLYSES OF 1-CHLORONITROSOCYCLOHEXANE AND -PENTANE IN 50:30:20 ACETONITRILE, WATER, ETHANOL (VOLUME) AT 50.0

Initial concentrations, mole/l. [Chloronitrosoalkane]	[AgClO$_4$]	Second-order constant, l./mole-min. × 10^2
0.200[a]	0.099	2.06
.199[a]	.159	1.84
.200[a]	.300	2.03
.199[a]	.310	2.11
.199[a]	.416	2.30
.200[b]	.305	4.92
.200[b]	.149	4.97
.201[b]	.164	4.87
.201[b]	.100	4.97
.207[b]	.400	5.23

[a] 1-Chloronitrosocyclohexane, mean $k_2 = 2.07 \pm 0.23 \times 10^{-2}$ l./mole-min. [b] 1-Chloronitrosocyclopentane, mean $k_2 = 5.08 \pm 0.16 \times 10^{-2}$ l./mole-min.

It is seen from these results that the cyclopentane derivative is approximately 2.5 times as reactive as the cyclohexane derivative under these experimental conditions.

Several reactions were carried out under kinetic conditions and the products examined. It was found that both the cyclopentyl and cyclohexyl derivatives gave quantitative yields of silver chloride and 85 and 92% yields of the corresponding ketone (isolated as 2,4-dinitrophenylhydrazones), respectively. The reaction mixtures were found to evolve no gas during the reaction. Similarly, no nitrogen dioxide or nitric oxide was observed in either case as evidenced by the absence of brown fumes above the reaction mixture. Hydroxylamine was shown to be absent by treating a portion of the reaction mixtures with an acidic solution of ferric chloride[6] followed by titration of the resulting ferrous ion with standard potassium permanganate solution. In no case was more than a trace of ferrous ion produced. Vapor phase chromatography[7] of a portion of each reaction mixture at −78° gave a single large peak for a soluble gas present in high concentration and with the characteristic retention time of nitrous oxide. Although these latter experiments were not quantitative in nature, the complete absence of other nitrogen-containing compounds in the reaction mixture supports the view that nitrous oxide is the only nitrogenous product.

Discussion

The fact that the reaction of silver perchlorate with 1-chloronitrosocyclohexane and 1-chloronitrosocyclopentane in aqueous ethanolic acetonitrile obeys the kinetic equation 1 over a range of silver salt concentrations leads to the conclusion that silver ion functions as the electrophilic reagent, solvent as the nucleophile[8] and that perchlorate ion is not kinetically involved.[9] Furthermore, the fact that the cyclopentane derivative is 2.5 times as reactive as the cyclohexane derivative under the same conditions lends considerable support to the idea that a displacement reaction on carbon is the rate-determining process.[10]

Granted that an α-hydroxynitrosoalkane is formed *in situ* as the product of this rate-determining displacement reaction, the reaction products arising from the decomposition of this intermediate may be rationalized in terms of the reaction sequence 3 which was proposed as an integral portion of the Nef reaction sequence.

Further evidence for reaction sequence 3 is to be found in the recently reported work of Iffland and Criner.[11] These authors report that cyclohexanone oxime reacts readily with lead tetraacetate to produce a blue liquid which appears to be 1-acetoxnitrosocyclohexane. Hydrolysis of this ma-

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[5] E. Muller, H. Metzger and D. Fries, *Ber.*, **87**, 1449 (1954); **88**, 1891 (1955).

[6] N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 647.

[7] We are indebted to Dr. Charles B. Colburn for performing these experiments.

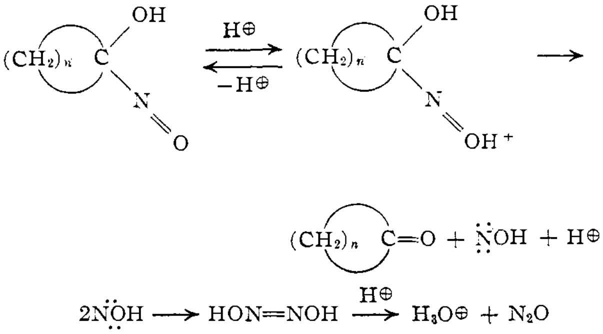
[8] Although a mixed solvent was used in the kinetic and product experiments, the approximately 4:1 mole ratio of water to ethanol present in that solvent mixture would probably make water the dominant product-determining nucleophile in these reactions. It should be pointed out that if ethanol is the nucleophile which initially attacks the substrate, the product which seems likely to arise from this attack may revert, by acid-catalyzed hydrolysis, to the products formed by the direct attack of water.

[9] The observed kinetics do not distinguish between this situation and that situation which would exist if silver perchlorate were completely associated and both silver ion and perchlorate ion entered into the rate-determining transition state. This latter situation is most improbable due to the ionizing power of the solvent mixture.

[10] H. C. Brown and G. Ham, THIS JOURNAL, **78**, 2735 (1956).

[11] D. C. Iffland and G. X. Criner, *Chemistry & Industry*, 176 (1956).

terial in aqueous acid media produces a quantitative yield of cyclohexanone. It seems reasonable to assume that the first step of this hydrolysis is the formation of 1-hydroxynitrosocyclohexane which further decomposes as in 3. Although the authors did not isolate or identify nitrous oxide, its presence in the reaction products is indicated.



(3)

Experimental[12]

1-Chloronitrosocyclopentane was prepared in 75% yield by the method of Muller, Fries and Metzger[5] and fractionated with a 20-plate Heli-pak column at 15 mm., b.p. 42° and $n^{20}\mathrm{D}$ 1.4570 (lit.[5] $n^{20}\mathrm{D}$ 1.4570).

1-Chloronitrosocyclohexane was prepared and distilled in a like manner[5] at 15 mm., b.p. 55°, $n^{20}\mathrm{D}$ 1.4630 (lit.[5] $n^{20}\mathrm{D}$ 1.4629).

Acetonitrile was obtained from the Union Carbide and Carbon Co. and distilled from phosphorus pentoxide, b.p. 80°.

Ethanol was Union Carbide and Carbon C.P. absolute ethanol and the water used in the kinetic experiments was de-ionized conductivity water.

Silver perchlorate was chemically pure and obtained from the G. Frederick Smith Chemical Co. It was vacuum dried over phosphorus pentoxide before use.

Kinetic measurements were carried out in 10-ml. volumetric flasks which had been blackened with several coats of black paint. All kinetic measurements were carried out at 50.0 ± 0.01° in a solvent prepared by mixing 2 volumes of ethanol and 3 volumes of water with 5 volumes of acetonitrile. The following procedure was employed: an estimated amount of anhydrous silver perchlorate was placed in a 100-ml. volumetric flask and dissolved in *ca.* 100 ml. of solvent. Aliquots of this solution were taken and titrated for silver using standard ammonium thiocyanate and ferric alum indicator in dilute nitric acid. A predetermined weight of chloronitrosocycloalkane was weighed into a blackened 100-ml. volumetric flask and thermostated at 50.0°. The proper volume of standard silver perchlorate solution which had been previously thermostated was added and the reaction initiated by solution of the chloronitrosoalkane and the time noted. Several 10.0-ml. aliquots of reaction mixture were immediately transferred to thermostated 10-ml. volumetric flasks. At various time intervals a sample flask was withdrawn, its contents washed into 20 ml. of distilled water covered by 10–15 ml. of hexane. The hexane completely separated the blue nitroso compounds from the aqueous phase and allowed the produced acid to be titrated to the brom thymol blue end-point with standard, 0.10 *N* sodium hydroxide. The resulting acid titer was used in the calculation of the instantaneous concentrations of silver perchlorate and chloronitrosoalkanes, and these values were treated as in Fig. 1. In every case the reactions were carried to at least 50% completion. Spectrophotometric control experiments carried out at 620 mμ and in the reaction solvent at 50.0° showed that not more than 1–2% of chloronitrosoalkane decomposed during the course of the longest kinetic run. In one kinetic experiment it was found that the acid titer agreed with the quantity of silver chloride to within 2% at 50% reaction.

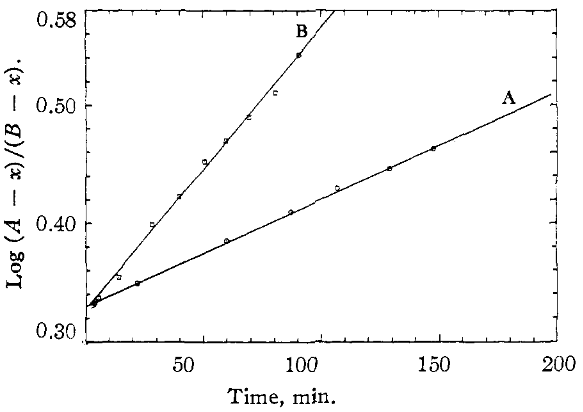


Fig. 1.—Second-order plot of the reaction of 0.100 *M* silver perchlorate with 0.20 *M* 1-chloronitrosocyclohexane, A, and 0.20 *M* 1-chloronitrosocyclopentane, B.

Product analyses were carried out for silver chloride, hydroxylamine, ketone and nitrous oxide in the following manner: after the disappearance of blue color a reaction mixture originally prepared from 70 ml. of 0.40 *M* silver perchlorate and made up to 0.20 *M* with chloronitrosoalkane was filtered with a tared sintered glass funnel of medium porosity. The silver chloride so collected was washed with ethanol and then ether and air-dried. In every case the yield of silver chloride was found to be quantitative to within 1–2%.

The filtrate and combined washings were treated with a slight excess of aqueous 5% sodium chloride solution, to precipitate excess silver ion and the solid separated by filtration. The volume of the final filtrate (*ca.* 150 ml.) was determined and the solution divided into two equal portions. The first portion was treated with 2.5 g. of 2,4-dinitrophenylhydrazine hydrochloride and 5 ml. of concentrated hydrochloric acid and then heated for 1 hr. on the steam-bath. The mixture was then cooled to room temperature and the precipitated 2,4-dinitrophenylhydrazone separated by filtration, washed copiously with warm 5% aqueous hydrochloric acid followed by water and then air-dried. In this manner crude cyclopentanone and cyclohexanone 2,4-dinitrophenylhydrazones melting at 138–142°[13] and 156–160°,[13] respectively, were obtained in 85 and 92% yields, respectively.

The remaining half of the filtrate was reduced to *ca.* 20 ml. by low pressure evaporation and 1 g. of ferric ammonium sulfate and 5 ml. of concentrated sulfuric acid added. The resulting solution was refluxed for 5 minutes and immediately titrated with standard 0.1 *N* potassium permanganate solution. A permanent pink color was obtained on the addition of only 0.20 ml. of 0.0832 *N* permanganate showing the absence of hydroxylamine.[6]

Nitrous oxide was found to be present in a reaction mixture before work-up by placing 0.10 ml. of the solution on an infusorial earth gas chromatographic column having ethanol as a liquid phase. A chromatogram was obtained on this column using helium carrier gas and at −78°. Only a single peak was obtained and this had the characteristic retention time of nitrous oxide.[7] The absence of brown fumes and the lack of pressure increase during every experiment show that nitrous oxide was the only nitrogen-containing gaseous product.

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[12] All melting and boiling points are uncorrected.

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 221, report melting points of 142 and 166°, respectively.