5-Alkylaminotetrazoles. (A).—The guanidinium salt of the azomethine (0.05 mole) was dissolved in 100 ml. of absolute methanol or ethanol, by heating if necessary, and hydrogenated over 0.05 g. of Adams platinum catalyst at an initial pressure of 50 p.s.i. until the theoretical amount of hydrogen was absorbed. After the catalyst had been removed, the alcohol was evaporated and the residue dissolved in 100 ml. of hot water. The solution was then adjusted to *p*H 3–3.5 with concentrated hydrochloric acid, and cooled at 0° for several hours. The precipitated 5-alkylaminotetrazole was removed by filtration, washed with a small volume of cold water, and dried. The products were recrystallized from the solvents reported in Table II.

(B).—To a solution of 8.5 g. (0.1 mole) of anhydrous 5-aminotetrazole and 10.1 g. (0.1 mole) of anhydrous triethylamine in 50 ml. of absolute methanol was added 0.1 mole of the freshly distilled or neutral aldehyde. There was an immediate exothermic reaction due to the formation of the azomethine. This solution was hydrogenated and processed in the same manner as outlined under A. Because the formation of the azomethine was not quantitative under these conditions, the crude product frequently had to be washed several times with diethyl ether or ligroin to remove unreacted aldehyde or the alcohol resulting from its reduction.

Benzal-bis-(5-aminotetrazole).—Anhydrous 5-aminotetrazole (4.3 g., 0.05 mole) and 15 ml. of benzaldehyde, were heated to and maintained at 140–150° until a homogeneous solution was obtained and the evolution of water had ceased (about 15 minutes). When the solution had been cooled to room temperature, the product was removed by filtration and washed with benzene. The yield of dried material was 5.5 g., m.p. 160–165° when plunged into a hot bath. A sample for analysis was prepared by rapid recrystallization from benzaldehyde and was washed immediately with a large volume of petroleum ether until free of benzaldehyde; m.p. 190–192° dec. When plunged into a hot bath, the compound melts at 166–168°, resolidifies, then remelts at 187–188° (depends on heating rate). This compound hydrolyzes very readily. The analyses indicate a contamination with unreacted 5-aminotetrazole.

Anal. Calcd. for $C_9H_{10}N_{10}$: C, 41.85; H, 3.90; N, 54.24; equiv. wt., 129.13. Found: C, 40.06; H, 3.92; N, 55.89; equiv. wt., 133.9.

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Kinetics of the Alkaline Decomposition of 1,3-Dinitro-1,3-diazacyclopentane

BY WALTER H. JONES

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As part of an investigation, which has been indefinitely interrupted, of the alkaline decomposition of secondary nitramines, we here report the kinetics of the reaction of 1,3-dinitro-1,3-diazacyclopentane (hereinafter referred to as DDC) with methoxide ion in absolute methanol solution. This compound, prepared recently by Goodman,[1] is a simpler analog of cyclotrimethylenetrinitramine (hereinafter called RDX), which has been studied in a previous communication,[2] and it was hoped that the mechanism proposed there would be substantiated. Also, further investigation of this type of elimination reaction may be of theoretical interest.[3]

It was found that in absolute methanol DDC reacts with methoxide ion to provide quantitatively one mole of nitrite while consuming two moles of base. The rate of this reaction was investigated by determination of residual alkali and by analysis for nitrite. The kinetics were exceptionally clean throughout the course of the reaction (to about 90%), and experimentally identical rate constants were obtained by the two analytical procedures in terms of the mechanism

$$\mathrm{DDC} + (\mathrm{O\bar{C}H_3}) \xrightarrow{k} \mathrm{A} + \mathrm{CH_3OH} + (\mathrm{N\bar{O}_2})$$

$$\mathrm{A} + (\mathrm{O\bar{C}H_3}) \xrightarrow{\text{fast}} \mathrm{\bar{B}} + \mathrm{CH_3OH}$$

The kinetic results are summarized in Table I. A tenfold range of initial concentration ratios was employed, and no trend in rate constant was noted.

A plot of log (k/T) against $(1/T)$[4] gave a good straight line, and from the slope and intercept and their standard deviations[5] the activation quantities[6] $\Delta H^{\ddagger} = 29.51 \pm 0.04$ kcal./mole, $\Delta S^{\ddagger} = 17.10 \pm 0.11$ e.u. were obtained. These may be compared with the values of $\Delta H^{\ddagger} = 27.85 \pm 0.40$, $\Delta S^{\ddagger} = 23.6 \pm 1.3$ e.u. found for RDX.[2] At the common temperature employed, 44.93°, the RDX k_1 value was 4.08 ± 0.07 l. (mole min.)$^{-1}$. Hence, even allowing for a statistical factor of three in favor of RDX because of the greater number of acidic hydrogens available for attack, the RDX rate still exceeded that of DDC by 118 times and the difference was not predominantly in either the enthalpy or entropy of activation. If the initial reaction in both cases were an E2 elimination of nitrite, it might be speculated that the difference was due to an electrical effect of the additional nitramine group present in RDX or to greater ring strain associated with the transition state for DDC. Preliminary studies on the related open-chain compounds 2,4-dinitro-2,4-diazapentane and 5,7-dinitro-5,7-diazaundecane[7] indicated that these materials reacted considerably more slowly than the ring compounds. Dimethylnitramine showed no decomposition under the same conditions.

TABLE I

DDC KINETIC DATA

Temp., °C.	N[a]	k[b]
58.14 ± 0.05	4	0.0780 ± 0.0029
58.14 ± .05	5[c]	.0748 ± .0027
44.93 ± .01	4	.0115 ± .0001
72.86 ± .05	3	.543 ± .006
30.15 ± .02	2	.00131, 0.00128

[a] Number of rate runs. [b] Units: l. (mole min.)$^{-1}$. ± values are standard deviations of the mean. [c] $(\mathrm{O\bar{C}H_3})$ analysis; all others nitrite determinations.

Although we were unable to isolate and identify the reaction products (see Experimental), we may note that by analogy with the mechanism proposed for the RDX decomposition the intermediate A might be formulated as 1,3-diaza-3-nitrocyclopentene-1 (the alternative, 1,4-diaza-4-nitrocyclopentene-1, would require attack on the least acidic hy-

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(1) L. Goodman, THIS JOURNAL, **75**, 3019 (1954).

(2) W. H. Jones, *ibid.*, **76**, 829 (1954).

(3) W. H. Jones, *Science*, **118**, 387 (1953).

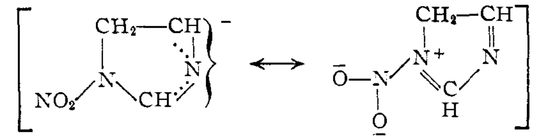
(4) According to the equation $k = (kT/h)e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941.

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

(6) In obtaining these quantities, the 30.15° data were not used, although they gave good straight-line agreement with the others, because it was only practical to study the first few per cent. of reaction at this temperature.

(7) Samples of these materials were kindly provided by Leon Goodman, to whom we wish to express our thanks.

drogen). The species $\bar{B}$ would then be written



Further elimination of nitrite, which was not observed, would give a salt of a tautomer of the very weakly acidic imidazole. Hence none of the results was inconsistent with the previously proposed mechanism, although the latter was not of course by any means proved.

Experimental

A sample of DDC was generously supplied by Leon Goodman, and further quantities were prepared and purified by his method B.[1]

Rate Measurements.—The solvent, nitrite analysis, method of preparing solutions, thermometer and constant-temperature baths have been described previously.[2] Alkali determinations were carried out by phenolphthalein titration or by a potentiometric procedure using a Beckman Model H-2 glass electrode *p*H meter; identical results were obtained by the two methods. Frequently, particularly late in the reaction, the alkali end-points were slow to become permanent. The usual sealed ampoule technique was employed; for the higher temperature runs the tubes were cooled in an ice slush before sampling, the appropriate density corrections being made. Initial concentrations ranged from 0.003 to 0.055 *M*. Under the experimental conditions, no solvolysis reaction could be detected. Rate constants were obtained from appropriate plots of the equations

$$\frac{1}{(2b-a)}\ln\frac{a(z+2b-a)}{2bz} = kt$$

$$\frac{1}{(2b-a)}\ln\frac{a(b-x)}{b(a-2x)} = kt$$

where a = initial concentration of $(\bar{O}CH_3)$, b = initial concentration of DDC, k is the specific rate of production of nitrite, and x and z are the $(N\bar{O}_2)$ and $(\bar{O}CH_3)$ concentrations at time t.

Reaction Product.—On passing the alkaline reaction solution through a Dowex-50 ion-exchange column, heating the effluent with urea, evaporating to dryness and extracting with chloroform, a water-soluble strong acid, m.p. 57°, was obtained in very small (2%) yield. It gave a positive Franchimont[8] nitramine test using 1-naphthylamine. Equivalent weight determinations on this material (phenolphthalein end-point) gave 173, 175 and 178 g./eq. The equivalent weight of a urea adduct of the postulated compound A is 175. The C, H, N, analyses did not, however, check with this structure or any simple empirical formula. Other attempts to isolate a reaction product were wholly unsuccessful.

Acknowledgment.—The writer wishes to thank Richard G. Thrap for help with some of the preliminary kinetic experiments.

[8] A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 226 (1897).

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Rapid Exchange between Iodine and Stannic Iodide in Carbon Tetrachloride at 0°[1]

BY MILTON KAHN AND ARTHUR J. FREEDMAN

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This paper deals with the rapid exchange between stannic iodide and iodine in carbon tetrachloride at 0° in the presence of a dark red light. Stannic iodide was separated from iodine by precipitation with pyridine. It was found that under the foregoing conditions, complete exchange occurred in less than seven seconds, the minimum time required to perform the chemical separation. Since polyvalent metal halides are known to react with halogens in organic solvents to form positive halide ions,[2] it is possible that such a mechanism may account for the rapid exchange observed in this instance.

Experimental

Stannic iodide was prepared by heating A.R. grade tin with excess iodine in a sealed tube. The resulting material was first treated with dry nitrogen to remove excess iodine, and a portion was subsequently distilled in vacuum.

Mallinckrodt A.R. grade carbon tetrachloride was purified according to the method of Fieser,[3] and was treated with dry, oxygen-free argon for eight hours before use. Mallinckrodt A.R. grade iodine and pyridine were used without further purification, and "carrier-free" radioactive I^{131} was obtained from the Atomic Energy Commission.

A $1.10 \times 10^{-3} f$ solution of iodine in carbon tetrachloride was activated by shaking with an aqueous solution containing I^{131} activity plus a trace of potassium iodide carrier, and was then carefully dried over Drierite. A $5.29 \times 10^{-4} f$ solution of stannic iodide in carbon tetrachloride was prepared just before use, taking care to exclude oxygen by flushing the volumetric flasks with argon, and both solutions were cooled to 0° in an ice-bath.

Four milliliters of the iodine solution was transferred to a 10-ml. extraction vessel and stirred with a stream of argon. Two milliliters of the stannic iodide solution was added, followed as rapidly as possible (seven seconds) by 0.05 ml. of pyridine. Pyridine is reported[4] to form an insoluble complex with stannic iodide containing two moles of pyridine per mole of stannic iodide. However, it was found that the precipitate formed as described above was not quantitative and carried an appreciable amount of iodine and, therefore, in order to determine the fraction exchange it was necessary to ascertain the composition of the precipitate. This determination was accomplished in the following manner. The precipitate was dissolved in 0.5 *f* sulfuric acid and the molecular iodine extracted with carbon tetrachloride. The supernatant liquid was extracted with 0.5 *f* sulfuric acid. All phases were separated by centrifugation and counted.

Assuming that during each of the above extractions complete exchange occurred between iodide ion in the aqueous phase and molecular iodine in carbon tetrachloride,[5] it is possible to calculate from the experimental data the composition of the precipitate and subsequently the fraction exchange. The experimental results are summarized in Table I. In these experiments the preparation of the stannic iodide solution and all steps in the exchange reaction includ-

TABLE I

Reacn. mixt.,[a] mole × 10^6	SnI_4	1.06	1.06
	I_2	4.40	4.40
Precipitate,[b] mole × 10^6	SnI_4	1.00	1.01
	I_2	2.02	2.02
S_∞[c] × 10^{-10}		3.16	2.88
S_t[d] $_{= 7 \text{ sec.}}$ × 10^{-10}		3.12	2.90

[a] Composition of reaction mixture: $1.76 \times 10^{-4} f$ SnI_4, $7.33 \times 10^{-4} f$ I_2. [b] Values are corrected for coincidence losses and for the distribution of iodine between carbon tetrachloride and the aqueous phase. [c] S_∞ = specific activity of total iodine in the reaction mixture. [d] $S_{t = 7 \text{ sec.}}$ = specific activity of total iodine in the precipitate separated at time t = 7 sec.

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[1] This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 312.

[3] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 365.

[4] A. G. Dimitriou, *Praktica*, **2**, 496 (1927).

[5] D. Hull, C. Shiflet and S. Lind, THIS JOURNAL, **58**, 535 (1936); F. Juliusberger, B. Topley and J. Weiss, *J. Chem. Phys.*, **3**, 437 (1935).