oxide was always well under 15%. (3) A standard solution of PBP was left at 50° until all peroxide had disappeared. Excess hydroperoxide was then added, and then a sample of halide. No difference could be detected in the rate of reaction due to the decomposition products. (4) As in (3), except no additional peroxide added. The rate of reaction of the decomposition products with halide is about one-half of the peroxide ion. (5) The excellent linearity of the second-order plots up to nearly complete reaction precludes the possibility that we are studying competing reactions unless they have identical rates.

ALBANY, CALIF. RECEIVED SEPTEMBER 12, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Direction of Addition to $CFCl{=}CF_2$ under Free Radical Conditions[1]

BY ALBERT L. HENNE AND DOROTHY W. KRAUS

In the presence of a peroxide, or in ultraviolet irradiation, $CFCl{=}CF_2$ accepts CF_3I or CCl_3Br to yield $CF_3CFClCF_2I$ or $CCl_3CFClCF_2Br$, respectively. To prove these formulas, $CF_3CFClCF_2I$ was transformed to $CF_3CF{=}CF_2$ by means of zinc; $CCl_3CFClCF_2Br$ was fluorinated to $C_3F_6Cl_2$ which, by treatment with zinc, also gave $CF_3CF{=}CF_2$. If addition had taken place in the opposite direction, neither adduct could have given $CF_3CF{=}CF_2$.

Under free radical conditions, $CF_2{=}CF_2$ accepts CF_3I to make $CF_3CF_2CF_2I$; the reaction is pictured as promoted by the $CF_3\cdot$ radical, with chain formation of an intermediate $CF_3(CF_2CF_2)\cdot$, and termination by an iodine atom. Promotion by $CF_3\cdot$ rather than $I\cdot$ is, however, merely postulated, not demonstrated.[2]

With an asymmetrically fluorinated olefin, the direction of addition must be experimentally determined, and this additional information may help to establish the reaction mechanism. For this purpose, CF_3I was added to $CFCl{=}CF_2$, and it was found that the C_3 part of the adduct must be formulated as $CF_3CFClCF_2I$ because its reaction with zinc in alcohol gave nothing but the known[3] $CF_3CF{=}CF_2$; had the addition occurred in the opposite direction, CF_3CF_2CFClI would have been formed, which could not have been transformed to C_3F_6 by means of zinc.

It is therefore an established fact that the CF_3 group links to the CFCl side of $CFCl{=}CF_2$. If it is postulated by analogy that the reaction is initiated by a $CF_3\cdot$ radical, an intermediate CF_3-$CFClCF_2\cdot$ is formed in preference and possibly to the exclusion of $CF_3CF_2CFCl\cdot$; since it is known from electron diffraction patterns that the bond joining a CF_2 group to another atom is shorter than that involving a CFCl group, an intermediate $CF_3CFClCF_2\cdot$ would represent formation of a weaker C–CFCl bond in preference to a stronger C–CF_2 bond.

For confirmation, the addition of CCl_3Br to $CFCl{=}CF_2$ was investigated under conditions favoring free-radical reaction. The C_3 fraction was isolated, subjected to conventional fluorination with antimony fluoride and thus transformed into $C_3F_6Cl_2$; the latter, treated with zinc in alcohol under pressure, gave only one product, the known C_3F_6, and must therefore have been $CF_3CFClCF_2Cl$. This in turn means that in the original addition, a CX_3 group became linked to the CFCl side of $CFCl{=}CF_2$ and parallels the result obtained with CF_3I. Because no compound corresponding to a reversed addition was isolated, it is submitted that the addition may have occurred in one direction only.

A third set of experiments encountered so much side-reacting that it could not be utilized as a confirmation, but it gave qualitative indications which were not at variance with expectations. The addition product from CCl_3Br and $CFCl{=}CF_2$ was treated with zinc in the hope of forming (and isolating) an olefin $C_3F_3X_3$ and ZnX_2 if its middle group was CClF, or else $C_3F_2X_4$ and ZnFX if the middle group was CF_2. Much decomposition took place, which robbed a fluoride ion test of its significance; the olefin apparently underwent further reaction and the main by-product seemed to be $C_6F_6Cl_2$.

Experimental

Addition of CF_3I.—An equimolecular mixture of CF_3I[4] and $CClF{=}CF_2$ (0.2 mole each) was placed in the previously described[5] mercury arc equipped container, and maintained under reflux by means of a Dry Ice condenser for a period of 54 hours. The unreacted material, amounting to $^3/_4$ of the batch, was then recovered by low temperature distillation as a mixture boiling around −25°; the remaining $^1/_4$ was left as a liquid residue boiling above room temperature. All of this liquid was treated with zinc in absolute alcohol, and thus transformed into a gaseous material which was caught in a Dry Ice trap; the alcohol solution did not retain more than traces of an organic halide, and a test for fluoride ions proved negative, while a test with silver nitrate gave a voluminous precipitate. The liquefied gas was found to boil at −28°, which is correct for C_3F_6, and it accepted chlorine to yield a compound boiling at 35°, with a refractive index $n^{20}\text{D}$ 1.3041, properties which agree with those of the known $CF_3CFClCF_2Cl$.

In another test, an equimolecular mixture of liquefied reagents (0.15 mole each) was sealed in a 1-liter quartz flask, and illuminated with an ultraviolet lamp for 4 weeks. After distilling the unreacted materials, a small amount of liquid (4 to 5 cc.) was collected, treated with zinc in alcohol as above, and the resulting gas chlorinated to yield a liquid (2–3 cc.) b.p. 35°, $n^{20}\text{D}$ 1.3047; no other product was seen and a fluoride ion test after the zinc reaction was negative. These results qualitatively parallel those of the preceding test.

In subsequent tests, mixtures of CF_3I and $CF_2{=}CFCl$ of varied compositions were heated to 85° with small amounts of benzoyl peroxide. Polymerization predominated in all cases, with formation of $CF_3(CF_2Cl)_nI$, from which a monomer could not be isolated.

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[1] Presented at the Chicago Meeting of the American Chemical Society, September, 1950.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949).

[3] A. L. Henne and T. P. Waalkes, THIS JOURNAL, **68**, 496 (1946).

[4] A. L. Henne and W. G. Finnegan, *ibid.*, **72**, 3806 (1950).

[5] A. L. Henne and E. G. DeWitt, *ibid.*, **70**, 1548 (1948).

Addition of CCl_3Br.—A mixture of CCl_3Br (1200 g. or 6 moles), benzoyl peroxide (6 g.) and $CFCl{=}CF_2$ (215 g. or 2 moles) was shaken in an autoclave. The temperature was slowly raised to 85° in about 2 hours, and during this period the pressure rose to a maximum of 7 to 8 atmospheres after which it dropped progressively to 2.5 to 3 atmospheres in about one-half hour, then fell to zero when the autoclave was brought to room temperature. The reacted mass was subjected to distillation; as soon as most of the excess of CCl_3Br was removed, the pressure was lowered to 6 mm. and by continued distillation a fraction of crude $C_3Cl_4F_3Br$ (285 g. or 45% yield) was collected, with b.p. 58–63° at 6 mm., $n^{20}\mathrm{D}$ 1.4673 to 1.4643. Next came a fraction $C_6Cl_5F_6Br$, b.p. 104–115° at 6 mm., $n^{20}\mathrm{D}$ 1.4532, and a residue, $n^{20}\mathrm{D}$ 1.4455, which were discarded.

Fluorination to $C_3F_5Cl_3$.—Part of the C_3 obtained in the above addition (131 g. or 0.41 mole) was heated with SbF_3Cl_2 (200 g. or 0.8 mole) at 100° for 48 hours in a rocking autoclave. Distillation gave 78 g. of a product b.p. 72°, which is an 80% yield if it is assumed that the reaction product is $C_3F_5Cl_3$.

Fluorination to $C_3F_6Cl_2$.—The above product ($C_3F_5Cl_3$, 78 g. or 0.38 mole) was mixed with fresh SbF_3Cl_2 (65 g.), and heated in a shaking autoclave at 150° for 48 hours. Distillation gave 62 g. of a product boiling 34 to 36°, $n^{20}\mathrm{D}$ 1.3044, which is an 85% conversion on the basis of the reaction product being $C_3F_6Cl_2$.

Dechlorination to $CF_3CF{=}CF_2$.—The preceding product (62 g. or 0.28 mole) was mixed with an equal volume of absolute ethanol, sealed in an autoclave containing 20.2 g. of granular zinc and shaken overnight at 100°. Distillation gave 25 g. of a product b.p. −29°, which is a 59% conversion on the basis of $CF_3CF{=}CF_2$.

Attempted Dehalogenation of $C_3Cl_4F_3Br$.—This reaction was attempted in the hope that the addition product of CCl_3Br and $CFCl{=}CF_2$ would yield a mixture of $CCl_2{=}CFCF_2Br$ and $CCl_3CF{=}CF_2$ if its formula were $CCl_3CClFCF_2Br$, but would not react (at least not without loss of fluorine) if it were $CCl_3CF_2CFClBr$. The reaction with zinc occurred very readily, but the reaction products were a complex mixture instead of the expected propenes, in which the main constituent seemed to be a compound, b.p. 170°, presumed to be $CF_2{=}CFCCl{=}CClCF{=}CF_2$. This type of "doubling up" has been observed before.[6,7] Titration of the mixed chlorine and bromine ions in the solution corresponded to the quantity of zinc consumed, while a test for fluorine ions was only very faint.

The operating conditions were then modified by feeding $C_3Cl_4F_3Br$ to an agitated suspension of zinc in boiling alcohol; by adjusting the water flow in the reflux condenser, it became possible to allow an azeotropic mixture of alcohol and olefin to distil through, while most of the saturated halide was returned to the reaction. The distillate was washed with water, dried and distilled to yield only two fractions, the first of which boiled 32–35° at 25 mm., $n^{20}\mathrm{D}$ 1.4212, and was regarded as the desired olefin, while the second one b.p. 68–72° at 25 mm., $n^{20}\mathrm{D}$ 1.4644, was clearly recovered starting material. As the olefin was formed without loss of fluorine, it was held that a central CFCl group must have been present in the starting compound.

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(6) E. J. Young, Ph.D. dissertation, The Ohio State University, 1947.

(7) A. L. Henne, J. W. Shepard and E. J. Young, THIS JOURNAL, **72**, 3577 (1950).

COLUMBUS, OHIO RECEIVED AUGUST 30, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

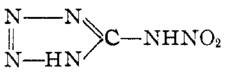
The Comparative Acidic Properties of Some 5-Substituted Tetrazoles

BY EUGENE LIEBER, SEYMOUR H. PATINKIN AND HSIANG HSIA TAO[1]

The effects of substituents in the 5-position of the tetrazole ring have been determined potentiometrically. The substituents examined were hydrogen, chlorine, bromine, iodine, amino, azide and nitroamino. The potentiometric behavior of nitroguanyl azide, the open chain isomer of 5-nitroaminotetrazole, is also reported. Substitutions in the 5-position of the tetrazole ring have an effect which is quite analogous to that found in ortho-substituted benzoic acids, the acidities increasing in the order $-NH_2$, $-H$, $-I$, $-Br$ and $-Cl$, with the azido and nitramino groups having unusual effects which cannot be explained by the electronegativity properties associated with those groups. 5-Nitroaminotetrazole is a dibasic acid, the acidity of the first proton being comparable to strong mineral acids, that of the second proton having a value of approximately 10^{-7}. The comparative acidic properties of some similarly constituted 1,2,4-triazoles are presented and discussed.

Introduction

The strong acidic properties of 5-nitroaminotetrazole[2] (I) had previously been noted[3] qualitatively by means of indicators.

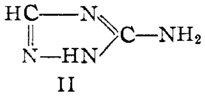

I

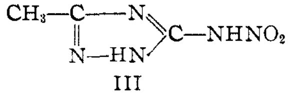
In order to define more precisely the effect of substitution on the tetrazole ring the comparative order of acidities and approximate dissociation constants of 5-chloro, 5-bromo, 5-iodo, 5-amino, 5-hydrogen (tetrazole), 5-azido and 5-nitroaminotetrazole, together with the mono-potassium salt of 5-nitroaminotetrazole, have been calculated from potentiometric measurements.

Of the large number of 5-monosubstituted tetrazoles that have been reported,[2] the acidic dissociation constants of only the 5-carbethoxy,[4] 5-amino,[5] 5-carboxamide[6] and tetrazole[6] have been determined.[7]

The dissociation constants of tetrazole and 5-aminotetrazole were redetermined in this paper, since the effect of an amino group upon the acidic properties of tetrazole seemed to be out of line in comparison with the effect of the same group on the acid properties of benzoic acid.

In order to determine the effect of altering the symmetry of the tetrazole ring by the introduction of a carbon atom in place of nitrogen on the acidity,


II


III

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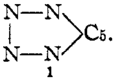
(1) Abstracted from a portion of the thesis submitted by Hsiang Hsia Tao to the Graduate School of the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

(2) The numbering scheme for the tetrazoles is  See F. R. Benson, *Chem. Revs.*, **41**, 1 (1947).

(3) E. Lieber, E. Sherman, R. A. Henry and J. Cohen, forthcoming publication.

(4) E. Oliveri-Mandala, *Gazz. chim. ital.*, **45**, II, 303 (1915).

(5) E. Bauer, *Z. physik. Chem.*, **23**, 409 (1897).

(6) E. Oliveri-Mandala, *Gazz. chim. ital.*, **44**, II, 175 (1914).

(7) After the submission of this paper for publication a report appeared by J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, **15**, 1082 (1950), presenting acidic dissociation constants for twenty-five alkyl- and aryl-5-substituted tetrazoles.