tion in certain amides is threefold: (1) it indicates that only one isomer is observed for most monosubstituted amides in the n.m.r. spectrum not because of rapid rotation about the C–N bond, but because of the preference for the *trans* configuration; (2) it shows that structural considerations, including nonbonded inter-

actions, play a part in determining the configuration about the peptide bond (this may also be important for polypeptide structures); and (3) it confirms the extensive infrared studies of N-methylformamide[10] which indicate that a small percentage of the molecules may possess the *cis* configuration.

Reactions of Active Nitrogen with Organic Substrates. II. Molecular Origins of Products of Reaction with Propene[1]

BY YOSHIHARU SHINOZAKI, ROBERT SHAW, AND NORMAN N. LICHTIN

The molecular origins of HCN, C_2H_2, C_2H_4, C_2H_6, C_3H_8, and CH_3CN formed by the reaction of active nitrogen with propene have been investigated by determining the relative molar radioactivities of these products when formed from propene-1-^{14}C, propene-2-^{14}C, and propene-3-^{14}C, respectively. The result establishes that none of these products arises by random utilization of the carbon atoms of the reactant. HCN originates more extensively in C-1 and C-3 than in C-2. Ethylene and CH_3CN appear to have the same precursor or precursors and are derived from C-2 plus C-1 and C-3 in the approximate ratio 2:1. Acetylene is derived from C-2 plus approximately equal proportions of C_1 and C_3. Ethane appears to be derived principally from C_1 and C_3. Propane is largely or solely formed by addition of hydrogen to propene. Mechanistic speculations are offered.

Introduction

Although the reactions of active nitrogen with organic molecules have, in recent years, been the subject of numerous investigations,[2-22] particularly in C. A. Winkler's laboratory at McGill University, there has been no report of studies directed toward identifying the chemical fate of individual atoms of a substrate molecule. This paper records our initial approach to securing such information by determining the molar radioactivities of the products of attack of active nitrogen on substrates suitably labeled with [14]C. Because each of its carbon atoms is structurally unique, propene is a convenient simple substrate and its three isomerically labeled forms were, accordingly, employed.

Experimental

General Procedures.—Reactions were carried out in an unpoisoned Pyrex flow system at ambient temperature and 4.2 mm. pressure. Purified molecular nitrogen, pumped at a rate of 149 ± 2 μmoles sec.$^{-1}$, corresponding to a linear flow rate of 232 cm. sec.$^{-1}$, was irradiated with 2450 Mc. microwaves to yield a nitrogen atom flow rate of 1.3 μmoles sec.$^{-1}$, as determined by the nitric oxide emission titration method.[23] Whether this method accurately measures nitrogen atom concentration has been ques-

tioned[20,24] but, under the fixed conditions of the present work, there is little question that the procedure provides a reliable relative measure. If, as Winkler and his co-workers suggest,[24] NO is also decomposed by $N_2(A^3\Sigma_u^+)$, then our application of the NO titration established that the sum and ratio of nitrogen atoms and $A^3\Sigma_u^+$ molecular nitrogen were constant throughout this work.

Propene was introduced at various flow rates with its direction of flow opposed to that of the nitrogen stream (cf. Fig. 1). The latter procedure gives a small sharply defined flame represented by F in Fig. 1. Products were trapped at liquid nitrogen temperature and separated by vapor phase chromatography. Yields were determined, rather roughly, by a combination of manometric data with chromatogram peak areas and area factors determined with authentic materials in this work. Products were identified by their infrared spectra.

The molar radioactivity of each product was determined, after its isolation and purification, by counting a known quantity in a sandwich type flow counter by the method of Christman and his co-workers.[25,26]

Materials of Research.—Nitrogen was Matheson "prepurified" grade and was further purified as described below. Propene-1-^{14}C were supplied by Research Specialties Co. while the 2-^{14}C isomer was from Nuclear Research Chemicals, Inc. Phillips Research Grade propene, which had been freed of air and water and which contained no other impurities detectable by gas chromatography, was used to dilute propene-1-^{14}C, -2-^{14}C, and -3-^{14}C to 0.25 μc./mM, 1.28 μc./mM, and 0.13 μc./mM, respectively. Undiluted propene-1-^{14}C and -2-^{14}C were analyzed for radioactive impurities by the methods used in analyzing reaction products. Propane and ethylene were the principal radioactive impurities, but their amounts and specific activities were too low to affect the results significantly. Nitric oxide (Matheson) was subjected to low temperature bulb-to-bulb distillation until no color was detectable in the gas phase.

Procedural Details.—Nitrogen, maintained at approximately atmospheric pressure by a mercury trap, was freed of O_2, H_2O, and CO_2 by passing it over copper turnings at 500°, cooling it in a water-jacketed tube, and trapping the condensables at liquid N_2 temperature. Flow rate was controlled at a capillary flow meter and measured at the exhaust side of the pump by means of a soap-bubble flow meter.

Active nitrogen was produced in a glow discharge generated with the full output of a Raytheon Model 10 microwave generator with a Type A medical antenna. Constancy of active nitrogen production in the unpoisoned system was achieved by pumping the system continuously when it was not in use and by conditioning the walls immediately before a run by passing active nitrogen until the afterglow intensities measured by photometers at P_1 and P_2 of Fig. 1 had fallen to constant values. The photometer at P_1 employed an A1P21 photomultiplier with a First Electronics Model 710-PR power supply and an RCA WV-84C d.c. microammeter. That at P_2 was an Eldorado Electronics Co. Model PH-200 equipped with a Model 200C 316 detector. It was established that interruption of the discharge for up to 1 min. did not

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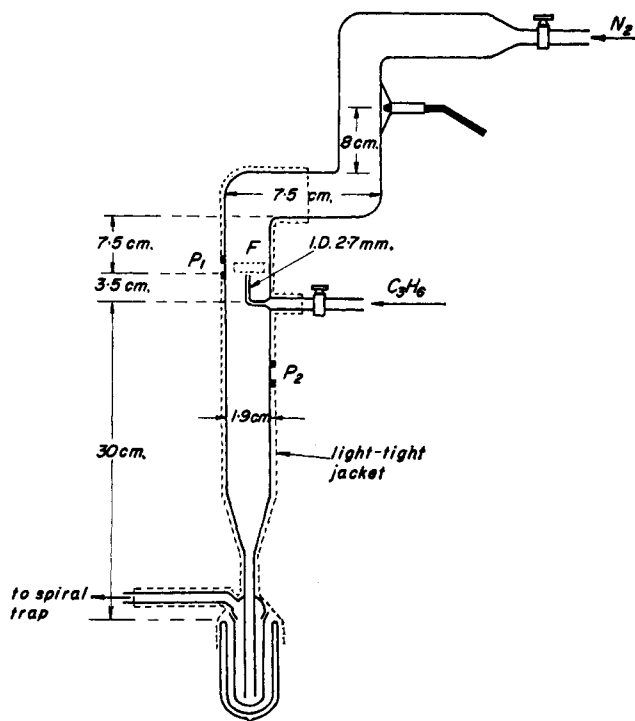(26) D. R. Christman and J. E. Stuber, *ibid.*, **28**, 1345 (1956).

Fig. 1.—Countercurrent reactor tube.

alter the afterglow intensity obtained on resumption of the discharge, once the plateau had been achieved.

The flow rate of atomic nitrogen at the plateau was determined[23] by allowing NO to flow from a reservoir through a capillary flow meter into the reactor and measuring the intensity of emission from the reaction flame with photometer P_1 as the flow rate of NO diminished through the equivalence point. Immediately before introducing reactant propene, the discharge was interrupted. Propene was then passed through the same flow meter for about half a minute until a constant flow rate was achieved. The discharge was then resumed and the reaction begun. Countercurrent mixing of the gas streams in the reactor shown in Fig. 1 gave a much more sharply defined flame than could be obtained by having the streams meet while flowing in the same direction and was employed throughout this work.

Unreacted propene and reaction products were collected at liquid nitrogen temperature in two traps, the second of which consisted of a spiral made of 60 cm. of 9-mm. i.d. tubing. Methane was not trapped by this procedure. It was established that ethylene could be trapped with 80% efficiency. Products were distilled into a removable trap and transferred to the analytical system. Total volatile product was determined manometrically.

Gas chromatographic analyses, separations, and purifications were carried out on didecyl phthalate in a 4-ft. metal column and on silica gel in a 3.8-ft., 4-mm. i.d. glass column using Matheson helium, freed of CO_2 and water by trapping at liquid nitrogen temperature, as carrier gas. Constancy of helium flow through a column and the reference side of the thermal conductivity cell was maintained by regulating the inlet pressure as indicated by Hoke Bantam flow gages. The thermistor equipped thermal conductivity cell was maintained at $25 \pm 0.2°$ and its output was fed through an attenuator into a Texas Instrument Co. dual channel two-pen Model WD Servo-riter.

About 50 μM at a time of the reaction product was first separated on didecyl phthalate into hydrocarbon, HCN, and nitrile fractions which were collected at liquid nitrogen temperature. The HCN and nitrile fractions were purified on the same column while separation and subsequent purification of the hydrocarbons were carried out on silica gel. Relative losses of HCN and propylene were sufficiently small during separation to permit manometric determination of their yields. Yields of the other products were calculated from the manometrically determined yields of the initial three fractions and chromatogram peak areas of individual components with the aid of area factors determined under identical conditions with authentic samples of the various products. All molar activity data were determined using manometrically determined amounts of isolated products which had been purified by repeated chromatography.

Samples were swept from the chromatographic columns into a sandwich type flow counter by the stream of helium. The Mylar window equipped with brass and Teflon counter[27] (Atom.

Mech. Machine Co.) employed P-10 counter gas (Matheson) and was shielded by 2 in. of lead. Other counting equipment included a Nucleonic Corp. Model RCR 3 scaler-ratemeter, the output of which was fed through an attenuator to the recorder, a Cosmic Radiation Laboratories Model PA 201 preamplifier, and a Raytheon Model VR6115 voltage stabilizer. The counter efficiency was determined with propylene, assuming the specific activity quoted by the suppliers, to be 28%, in good agreement with the value, 30%, determined by Wolfgang and MacKay[27] using CO_2. Since counting rates for products and reactant were low, ranging from less than 25% of background to several times background, the background correction required great care. The use of the Servo-riter to record the output of the scaler proved unsatisfactory; background corrections were too dependent on baseline stability, for instance. The recorder was therefore used only to indicate the passage of a radioactive compound through the counter. The activity data reported herein were obtained by using a Polaroid Model 900 camera to photograph the scaler dials before, during, and after the passage of a sample through the counter. This method permitted more precise determination of effective background and appeared to be successful. Inaccuracies in the data are known to have arisen from difficulties in the procedures employed in transferring product aliquots and in technical aspects of the counting equipment. Actually flow counting is not necessary in the procedure evolved and improved results with static counting are anticipated.

Data

Results are summarized in Tables I–III. The data of each horizontal line in Tables I and II are derived from a single experiment. In some cases two or more aliquots of a given isolated product were counted, as were several aliquots of each reactant propylene, giving mean deviations for a given material which were normally in the range from 1 to 5%. The data of Table III make clear, however, that the over-all accuracy of the results is considerably poorer than the precision of counting. Since the origins of the discrepancies between theoretical and observed values of the sums of relative molar activities are on the whole not known, it is dangerous to impute too much significance to any single datum. The very large discrepancies observed for ethane are probably a consequence of imperfect separation from ethylene, a much more abundant product with a similar chromatographic retention time. This source of uncertainty was minimized for propene-2-^{14}C, the last substrate to be investigated.

Polymeric material is also formed in the reaction of propylene with active nitrogen but was not subjected to systematic investigation. One sample after exposure to air was found to contain 4.3% hydrogen, 45.0% carbon, and 36.7% nitrogen.[28]

The uncertainty which may possibly arise from identification of NO emission titration[23] data with atomic nitrogen flow rates is discussed briefly in the Experimental section. Regardless of the quantitative meaning of the data, the ratio of reactants used in our experiments was varied over a wide range which unequivocally includes both a ratio of less than one molecule of active species per molecule of propylene and a large excess of the former. If, as Winkler and his co-workers suggest,[20,24] NO is decomposed both by N and by $A^3\Sigma_u{}^+$ N_2 so that the NO titer is approximately twice[20] the concentration of atomic nitrogen, and if propylene reacts significantly only with atomic nitrogen, as has been suggested[20] for ethylene, then the ratios of reactants indicated in Tables I–III need only be divided by two (cf. the Discussion section for further consideration of this problem).

It is interesting to note that acetonitrile, which according to the present results is the second most abundant volatile product,[29] was not detected by prior workers.[6,30]

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TABLE I
PRODUCT YIELDS FROM UNLABELED PROPENE

$\frac{(N)}{(C_3H_6)}$	C_3H_6		HCN	C_2H_6	C_2H_4	C_2H_2	CH_3CN	C_3H_4	C_2H_3CN
	Supplied	Reacted							
0.37	195.5	36.4	18.6	0.7	5.3	$\sim$0	6.0	3.2	1.1
1.14	64.6	16.0	27.2	.3	3.7	0.6	4.4	2.2	0.8
6.1	11.0	9.8	8.1	.05	0.6	0.7	2.4	1.0	0.3

——μ moles/min.—— (column header over the product columns)

TABLE II
MOLAR ACTIVITIES OF PRODUCTS RELATIVE TO THOSE OF REACTANT PROPENES

$\frac{(N)}{(C_3H_6)}$	HCN	C_2H_6	C_2H_4	C_2H_2	CH_3CN	C_3H_4	C_3H_6
		From Propene-1-^{14}C					
0.27	0.36	1.11	0.69	...	...	0.97	...
1.20	.35	0.62	.60	0.45	0.69[a]	1.02	...
6.1	.30	.42	.59	.50	.57[a]	0.71	0.92
		From Propene-2-^{14}C					
0.39	...	0.15	0.75	...	...	0.92	1.00
1.19	0.24	.14	.85	0.83	0.84	.98	...
7.50	.22	.00	.88[b]	.87[b]	.79	.98[b]	1.00[b]
		From Propene-3-^{14}C					
0.37	0.40	...	0.29	...	0.25	0.93	...
1.14	.40	0.50	.27	0.48	.28	1.03	...
6.0	.32	.63	.36	.43	.41	0.91	0.93

[a] Determined on impure CH_3CN containing about 15% of CH_2=$CHCN$. [b] A leak occurred in the vacuum system on the day these products were counted. Experimental considerations indicated that all were contaminated with the same proportion of air. The raw values were therefore divided by 0.87 so as to normalize the value for propene to unity. This procedure is supported by the fact that three aliquots of standard propene-2-^{14}C, counted on the same day, before the leak was eliminated, had an apparent average activity equal to 90 ± 2% of the correct value. The correct value was obtained with an aliquot counted after elimination of the leak.

TABLE III
SUMS OF RELATIVE MOLAR ACTIVITIES IN PRODUCTS

$(N)/(C_3H_6)$	HCN	C_2H_6	C_2H_4	C_2H_2	CH_3CN	C_3H_4	C_3H_6
Theoretical	1.00	2.00	2.00	2.00	2.00	3.00	3.00
Found 1.2	0.99	1.26	1.69	1.76	1.81[a]	3.03	...
6.0-7.5	0.84	1.05	1.83	1.80	1.77	2.58	2.58

[a] Value ignores contamination of CH_3CN from propene-1-^{14}C by acrylonitrile.

Discussion

Molecular Origins of Products.—Although any single datum of Table II must be treated with caution, conclusions can be drawn from the total results. Clearly the atoms of reactant propylene are not distributed randomly in the products since, if they were, each two-carbon product would have a relative molar activity (hereinafter designated as A_R) of 0.67 under all conditions and regardless of the location of ^{14}C in reactant propene, while A_R of HCN would always be 0.33. Equally clearly, none of the C_2 products, with the possible exception of ethane (for which the data are least satisfactory), is derived from a unique pair of substrate atoms nor does HCN originate from a unique site.

The significance of the data for HCN is complicated by the fact that active nitrogen is known[2,31] to react with all the other tabulated products to form HCN. It might thus be expected that with increasing excess of active nitrogen the value of A_R for HCN should tend toward 0.33. The present data are equivocal because ΣA_R for HCN falls short of its theoretical value by 16% with large excess of active nitrogen. The low value of A_R obtained from propene-2-^{14}C with a large excess of active nitrogen is, however, supported by more recent work,[32] suggesting that under all the conditions of Table II the bulk of HCN is primary, *i.e.*, not derived from attack on other molecular products. The data

thus indicate that HCN is formed with some degree of selectivity from the terminal carbon atoms, regardless of their degree of saturation. It is interesting to speculate that the nearly equivalent degree of derivation of HCN from these carbon atoms suggests that an important reaction path involves an unstable intermediate in which C-1 and C-3 are equivalent.

The data for ethylene and methyl cyanide are remarkably similar at all ratios of reactants, even though the proportion of the latter is about four times greater with excess active nitrogen. The change in their relative abundance is consistent with the known[30,31] lower reactivity toward active nitrogen of CH_3CN. Ethylene and methyl cyanide thus appear to have the same precursor or precursors, and are derived in the main from C-2 plus either C-1 or C-3, the latter appearing in a ratio of approximately 2:1.

Ethane is clearly not formed in the main by addition of hydrogen to ethylene, even though it is formed in approximately constant proportion to the latter. Very little, if any, C-2 appears in ethane. The data are too uncertain to enable any conclusion to be drawn concerning the relative abundance of C-1 and C-3 in this product. Both, however, appear to be present to a significant degree.

The origin of acetylene resembles but is not identical to that of ethylene and methyl cyanide. As are the latter two, acetylene is composed of one C-2 per molecule but C-1 and C-3 contribute equally to the other atom. Again, as with HCN, there is a suggestion of an intermediate in which C-1 and C-3 have become equivalent.

Although a single datum, not known to be in error, deviates widely from the other A_R values for propane, the bulk of the data indicate that this product is formed solely, or nearly so, by addition of hydrogen to reactant propene. In no case do the data require that recovered propene be other than unreacted propene, *i.e.*, there is no evidence for resynthesis of propene from smaller fragments. The experiments described here are, however, incapable of detecting rearrangements within the propylene molecule, the occurrence of which further complicates interpretation of the results.

The Nature of the Reagent.—The construction of specific mechanistic models from information of the sort presented here requires that the nature of the attacking species be assumed. The situation is also complex in this respect since, in addition to ^4S nitrogen atoms[33] and excited molecular nitrogen in the $A^3\Sigma_u^+$ state,[20,34,35] other highly energetic species are probably present.[36] Even if the determination of ^4S atomic nitrogen by the nitric oxide emission titration method is valid,[37] the

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presence of other components of active nitrogen capable of attacking propylene is not thereby excluded. The present work unfortunately does not contribute to knowledge of the composition of active nitrogen.

Mechanistic Speculations.—It is pointed out above that C_2H_4 and CH_3CN appear to have a common precursor or precursors. It seems most probable that such a precursor would contain nitrogen, e.g., CH_2-CH_2 with an N bridge (I) in ground or excited states might be expected to undergo unimolecular or bimolecular rearrangement to CH_3CN and loss of N_2 at the wall or in a bimolecular reaction. At reduced concentration unimolecular rearrangement might predominate, a consideration which may be partially responsible for the roughly threefold increase in the ratio of $\overset{.}{C}H_3CN$ to C_2H_4 at lowest substrate concentration. The fact that C-1 preponderates over C-3 in these products suggests that at least some proportion of intermediate I results from attack on the original double bond of propylene. If the simplifying assumption is made that [4]S atomic nitrogen is the only significant reagent, then such initial attack can be visualized as proceeding via a relatively slow spin-forbidden addition to the double bond followed by rearrangement and loss of CH_2. An interesting alternative involves the concerted formation of monoradical I and diradical CH_2 in a process which conserves spin.

The deficiency of C-2 in HCN and the nearly equal contributions from C-1 and C-3 suggest a precursor in which the latter atoms become equivalent to each other but different from C-2. The necessary symmetry could be achieved, for instance, via initial spin-forbidden abstraction of hydrogen from C-3 followed by the fast reaction of the resulting allyl radical, presumably with atomic nitrogen, at its terminal atoms, associated with cleavage, or via formation of an unstable four-membered ring, followed by decomposition to HCN and other fragments. Alternatively, the indicated symmetry might be achieved by direct attack of nitrogen atom on propene to form an unstable four-membered ring, with loss or rearrangement of hydrogen. Similar processes are consistent with the indicated symmetry of the precursors of acetylene.

The present data are, of course, not capable of doing more than indicating the structural symmetries of the precursors of some of the products and the suggested precursors are only meant to be illustrative. It is not meant to imply that any of the observed products, with the possible exception of propane, is formed with a single reaction path.

Determination of Molecular Weights of Polynuclear Zirconium and Thorium Chelates by Nonequilibrium Ultracentrifugation[1]

By Richard L. Gustafson and Arthur E. Martell[2]

The degrees of aggregation of 1:1 Th(IV)–N-hydroxyethylethylenediamine triacetate (HEDTA), 1:1:1 Th(IV)–HEDTA–pyrocatechol 3,5-disulfonate (Tiron), 1:1 Zr(IV)–HEDTA, and 1:1:1 Zr(IV)–ethylenediamine tetraacetate (EDTA)–Tiron chelates have been calculated from data obtained by nonequilibrium centrifugation in sodium chloride solutions at 25°. The 1:1 Th(IV)–HEDTA chelate has been shown to be most probably hexameric, whereas solutions containing equimolar amounts of Th(IV), HEDTA, and Tiron to which have been added $4^2/_3$ and 6.0 moles of sodium hydroxide per mole of metal ion were shown to be polydisperse. Solutions of Zr(IV) and HEDTA at pH 6 were shown to be composed of mixtures of monomers and dimers. A value of $K_D = $ [dimer]/[monomer]$^2 = 10^{2.14}$ was obtained from the sedimentation data. The data obtained for the 1:1:1 Zr(IV)–EDTA–Tiron systems at pH 7 suggest that a mixture of monomers and dimers is present.

Introduction

Studies carried out by many workers have elucidated the nature of the hydrolysis and olation reactions of a large number of metal ions and metal chelates on the basis of potentiometric, spectrographic, polarographic, and ion-exchange data. However, in many cases, particularly those of highly charged metal ions, it has been impossible to determine the degrees of aggregation of the polymers which are formed. An important step in this direction was the adaptation by Kraus, Johnson, and co-workers of equilibrium ultracentrifugation measurements to the calculation of the degrees of polymerization of Zr(IV),[3,4] Hf(IV),[4,5] Bi(III),[6] In(III),[7] Au(III),[7] Hg(I),[7] Hg(II),[7] Pb(II),[8] and Sn(IV)[8,9]

ions at various pH and concentration levels. Subsequently, Gustafson and Martell[10] successfully adapted the methods of dealing with the ultracentrifugation of charged polymers as outlined by Johnson, Kraus, and Scatchard[11] to the Archibald[12] nonequilibrium technique as developed by Klainer and Kegeles[13] in order to determine the degrees of aggregation of 1:1 Th(IV)–diethylenetriamine pentaacetate and 1:1.5 Th(IV)–pyrocatechol 3,5-disulfonate (Tiron) systems. In the present study, the application of the nonequilibrium ultracentrifugation technique has been extended to 1:1 Th(IV)–N-hydroxyethylethylenediamine triacetate (HEDTA), 1:1:1 Th(IV)–HEDTA–Tiron, 1:1 Zr-(IV)–HEDTA, and 1:1:1 Zr(IV)–ethylenediamine tetraacetate (EDTA)–Tiron systems. Bogucki and Martell[14] have attempted to elucidate the structure of

(1) This work was supported by the U. S. Atomic Energy Commission under Contracts AT-(30-1)-1823 (Clark University) and AT-(11-1)-1020 (Illinois Institute of Technology).

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