

# Reactions of Active Nitrogen with Organic Substrates. III. The Degradative Products of the Reaction with 1,3-Butadiene<sup>1</sup>

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**Abstract:** Active nitrogen was produced by microwave supported glow discharge and was treated with 1,3-butadiene at autogenous temperature over a wide range of concentrations of reactants and N<sub>2</sub>. Fourteen "degradative" products, HCN, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>N<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, propene, allene, propyne, *n*-C<sub>4</sub>H<sub>10</sub>, *cis*-2-butene, *trans*-2-butene, CH<sub>3</sub>CN, and C<sub>2</sub>H<sub>3</sub>CN, were separated by gas chromatography and identified by infrared spectroscopy. Yields of nine of these were determined gas chromatographically under the various reaction conditions. The most salient feature of the data is the low sensitivity of the yield of HCN, the major product, to concentrations of reactants and N<sub>2</sub>. With the molecular ratio of C<sub>4</sub>H<sub>6</sub> to N(<sup>4</sup>S) (determined by NO emission titration) in the range 6.7 to 0.25 the conversion of N to HCN remains essentially constant at approximately 30%. With the ratio 0.12 the yield is 20%. The data appear to support a mechanism according to which the nine products which were studied in detail originate in a rate-determining addition of N(<sup>4</sup>S) to 1,3-butadiene followed by several parallel modes of unimolecular decomposition. It is suggested that a major portion of reactant N is converted back to N<sub>2</sub> via the reactions NH + NH → N<sub>2</sub> + H<sub>2</sub> and NH + N → N<sub>2</sub> + H. Yields of eight "monomeric" products which were reported previously<sup>3</sup> were determined over an extended range of conditions. The results are consistent with those previously reported and with the mechanism which is applicable to the "degradative" products.

The reaction of 1,3-butadiene in a gaseous flow system at ambient temperature with active nitrogen has been shown<sup>3</sup> to yield a large number of organic compounds. We have reported previously<sup>3</sup> on monomeric products, defined operationally as those substances which can be trapped at -78° and subsequently distilled at room temperature under a pressure of 10<sup>-2</sup> torr or less. These products are structurally monomeric in the sense that each has four to six carbon atoms in its skeleton. The approximate invariance of the relative rates of formation of eight principal monomeric products with substantial variation in concentrations of reactants and N<sub>2</sub> suggested that these products are formed by processes of identical kinetic order. We now report an analogous but more extensive investigation of the degradative products, defined operationally as those which are trapped at -196 but not at -78°. Additional study of the monomeric products is also described herein.

## Results

All reactions were carried out without external heating, *i.e.*, at the autogenous temperature of the reaction.

The glow discharge was produced with 2450-Mc microwaves from a Raytheon unit, Model KV-104(NB). The glass walls in the region of the reaction and trapping zone were cleaned periodically (to remove a film of polymeric material) by 5% aqueous hydrofluoric acid followed by distilled water, acetone, and prolonged pumping under high vacuum at room temperature. No wall "poisoning" substance was added. Routinely, the reaction system was pumped at 10<sup>-4</sup> torr or less for at least 10 hr and purged with active nitrogen for 0.5 hr before each reaction. The flow rate of atomic nitrogen

in the reactor was estimated by the NO emission titration method<sup>4</sup> with visual detection of the end point. This method remains controversial in spite of much relevant work.<sup>5,6</sup> It is possible that our estimates of N(<sup>4</sup>S) are as much as 35% too high. It must also be recognized that excited molecular nitrogen, *e.g.*, in the A<sup>3</sup>Σ<sub>u</sub><sup>+</sup> state,<sup>7</sup> may be a significant reactant in active nitrogen and that the content of this sort of reagent was not determined. Products were identified by infrared spectrometry and determined quantitatively by gas chromatography as detailed in the Experimental Section. All data are presented in the form of concentrations. These were calculated by dividing molar flow rates by the volume flow rate of N<sub>2</sub> at the pressure of the experiment. The latter was varied from 0.3 to 6.8 torr.

Identified products found in the "degradative" fraction include hydrogen cyanide, ethane, propane, butane, ethylene, propylene, *cis*-2-butene, *trans*-2-butene, allene, acetylene, propyne, acetonitrile, acrylonitrile, and cyanogen. Extensive information was collected concerning the dependence of nine of these, the C<sub>2</sub> and C<sub>3</sub> hydrocarbons, HCN and (CN)<sub>2</sub>, upon the concentrations of reactants. Only the yield of ethane appeared to be sensitive to the recent history of the reaction system, *i.e.*, to wall effects, presumably. Up to 30 times the normal yield was observed in experiments performed shortly after cleaning of the walls. Such results are excluded from data presented below. In general, yields of ethane were the least reproducible. Thirty-five experiments were performed to determine whether product yields depended on the period of the reaction, *i.e.*, whether a steady state was achieved. These experiments showed that steady-state production of the

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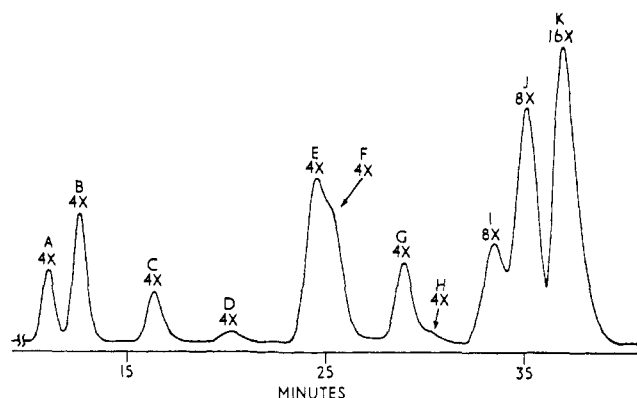


Figure 1. Vapor phase chromatograph of products of reaction with  $(C_4H_6)/(N) = 0.25$ ,  $(N) = 7.2 \times 10^{-7} M$ ,  $(N_2) = 3.2 \times 10^{-4} M$ , and linear flow rate =  $5.9 \text{ m sec}^{-1}$ . A =  $C_2H_6$ , B =  $C_2H_4$ , C =  $C_2H_2$ , D =  $C_3H_8$ , E = propene, F = allene, G =  $C_2N_2$ , H =  $N-C_4H_{10}$ , I = propyne, J = recovered 1,3-butadiene plus *cis*-2-butene, and K = HCN. Attenuator settings are indicated as factors of  $X$ .

principal hydrocarbon products  $C_2H_4$ ,  $C_2H_2$ ,  $C_3H_8$ , and allene was established in 0.5 min or less but that the rate of formation of HCN appeared to increase significantly during the first minute or so. This phenomenon did not significantly affect "integrated" yields of HCN in experiments of 4 min duration or longer and it is assumed herein that this apparent slower approach to steady-state production was an artifact of the trapping and transfer procedures for HCN. Typical data relevant to achievement of the steady state are presented in Table I. Similar data were also obtained with

Table I. Variation of Measured Product Yields with Reaction Period for  $(N)/(C_4H_6) = 1.0^{a,b}$

Reaction Period, min	$10^8 \times$ product yields, $M$						
	$C_2H_6$	$C_2H_4$	$C_2H_2$	Propene	Allene	$(CN)_2$	HCN
0.17		1.6	1.1	2.5	0.8		
0.50	0.4	1.8	0.8	3.2	0.9		9
0.75	0.2	2.0		3.9	0.8		14
1.0	0.2	2.0	1.2	3.6	1.0		16
2.0 <sup>c</sup>	0.2	1.8	1.2	3.4	0.8	1.1	18
4.0	0.1	1.7	0.9	3.3	1.0	1.0	21
8.0 <sup>d</sup>	0.1	1.7	1.2	3.4	1.2	0.9	23
120							21 <sup>e</sup>

<sup>a</sup> Pressure of  $N_2$ , 2.8 torr;  $(N) = (C_4H_6) = 8.1 \times 10^{-7} M$ ; linear flow rate,  $5.3 \text{ m sec}^{-1}$ . <sup>b</sup> Analyses by gas chromatography unless otherwise indicated; single experiments unless otherwise indicated. <sup>c</sup> Triplicate experiments; mean % mean deviation:  $C_2H_6$ , 3;  $C_2H_4$ , 7;  $C_2H_2$ , 10;  $C_3H_8$ , 7;  $C_3H_4$ , 15; HCN, 6. <sup>d</sup> Duplicate experiments; mean % mean deviation:  $C_2H_6$ , 5;  $C_2H_4$ , 4;  $C_2H_2$ , 6;  $C_3H_8$ , 1;  $C_3H_4$ , 22;  $C_2N_2$ , 5; HCN, 4. <sup>e</sup> Analysis by titration with silver ion (Liebig's method).

$(C_4H_6)/(N)$  equal to 6.7, 0.25, and 0.12. Yields of ethane under the latter conditions were constant or varied randomly with reaction period over a range comparable to that shown for this product in Table I. It is therefore assumed that the trend suggested by the data of Table I is not real.

The principal results of more than 100 experiments are presented in Table II. Each datum entered in the table is an average of results obtained for different reaction periods except for HCN. In the latter case the

data are taken from the plateaus of plots of yield vs. reaction time or, where less extensive data were collected, from reactions lasting 4 min or longer, except in a small number of cases where extrapolations were carried out. The amount of recovered butadiene was determined approximately for each experiment without rechromatographing. On this basis, consumption of butadiene was *ca.* 20% with  $(C_4H_6)/(N)$  equal to 6.7, *ca.* 35% with equal concentration of reactants, more than 80% with a ratio of 0.25, and more<sup>8</sup> than 90% with a ratio of 0.12.

Yields of monomeric products obtained in the present work are compared in Table III with those previously reported.<sup>3</sup> As in the earlier work, area factors were not determined and results are presented in the form of relative areas of product peaks.

A small number of determinations of acetonitrile and acrylonitrile with  $(N) = 10^{-6} M$  and  $(N_2) = 1.5 \times 10^{-4} M$  established that both products are formed when the ratio  $(C_4H_6)/(N)$  falls in the range from 0.25 to 7. The yield of acrylonitrile is substantial, greater than that of propylene, and about ten times that of  $CH_3CN$ . Acrylonitrile was also identified with the ratio  $(C_4H_6)/(N)$  equal to 0.12.

The production of *cis*-2-butene was established under a wide range of conditions with  $(C_4H_6)/(N)$  equal to 0.25 or 1.0, but this limitation may have been due to the difficulty of detecting it in the presence of a large excess of 1,3-butadiene. Since butadiene and *cis*-2-butene were not separated by the gas chromatographic procedure employed, quantitative yields of the latter were not determined. Butane was detectable gas chromatographically as a shoulder on the cyanogen peak but it can only be said that the yield was about an order of magnitude smaller than that of cyanogen (*cf.* Experimental Section). It was detectable in virtually all experiments with  $(C_4H_6)/(N)$  equal to 0.25 or 0.12 and in some with equimolar reagents.

The production of *trans*-2-butene was established by infrared spectrophotometry in two long-period experiments with  $(C_4H_6)/(N) = 0.12$ . *cis*-2-Butene appeared to be absent from the products of these experiments.

## Discussion

**Validity of the Data.** Replication of experiments under a large proportion of the conditions listed in Table II indicated that, for a given reaction period, yields of HCN,  $C_2H_4$ ,  $C_2H_2$ , and  $C_2N_2$  were reproducible to approximately  $\pm 10\%$ . Poor resolution of propylene and allene on the chromatograms (*cf.* Figure 1) substantially reduced the accuracy (as well as precision) of both these determinations. Precision of determination of propane was reduced by its small yield while that of propyne suffered from the incomplete separation of this compound from recovered butadiene. It has already been noted that yields of ethane, unlike other yields, appeared to be sensitive to wall conditions. The tabulated values are characteristic of the low yields obtained with aged walls. The data must be interpreted within these limitations on their quantitative significance.

**Types of Degradation Mechanism.** A possible source of part or all of the degradative hydrocarbon products is

(8) Since only the sum of recovered butadiene and *cis*-2-butene could be determined, only a lower limit to butadiene consumption can be given. This limit takes the amount of *cis*-2-butene to be negligible.

**Table II.** Ratios of Product Concentrations to Nitrogen Atom Concentrations at Different Reactant Concentrations

$10^7(\text{N})$ , $M$	$10^4(\text{N}_2)$ , <sup>a</sup> $M$	(Product)/(N)									
		HCN	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_2$	$\text{C}_3\text{H}_8$	Propene	Allene	Propyne	$\text{C}_2\text{N}_2$	
$(\text{C}_4\text{H}_6)/(\text{N}) = 6.7$											
8.2	1.5 <sup>b</sup>	0.29	0.002	0.031	0.014	+ <sup>h</sup>	0.058	0.010	...	+ <sup>h</sup>	
7.2	3.2 <sup>c</sup>	0.25	+ <sup>h</sup>	0.028	0.007	...	0.053	0.011	...	0.008	
7.2	2.4 <sup>c</sup>	0.28	+	0.031	0.008	...	0.056	0.012	...	0.008	
4.1	1.5 <sup>b</sup>	0.24	0.005	0.027	0.015	+	0.066	0.012	...	0.015	
3.3	0.59 <sup>d</sup>	0.32	+	0.033	0.014	+	0.082	0.009	...	0.015	
2.0	1.5 <sup>b</sup>	0.31	0.005	0.030	0.010	+	0.08	0.015	...	0.010	
1.6	0.40 <sup>e</sup>	0.23	0.006	0.04	0.013	...	0.08	0.019	...	0.013	
1.0	0.16 <sup>f</sup>	0.18	0.010	0.004	0.005	+	0.04	0.006	...	0.007	
$(\text{C}_4\text{H}_6)/(\text{N}) = 1.0$											
10.4	3.6 <sup>g</sup>	0.31	0.002	0.025	0.012	0.001	0.047	0.016	+ <sup>h</sup>	0.010	
8.2	1.5 <sup>b</sup>	0.28	0.001	0.022	0.014	+	0.042	0.011	..	0.012	
7.2	3.2 <sup>c</sup>	0.30	0.001	0.022	0.010	+	0.047	0.017	...	0.007	
7.2	2.4 <sup>c</sup>	0.32	0.001	0.024	0.011	+	0.050	0.015	...	0.011	
4.1	1.5 <sup>b</sup>	0.23	0.002	0.024	0.017	+	0.056	0.017	...	0.017	
3.3	0.59 <sup>d</sup>	0.25	0.006	0.012	0.009	+	0.036	0.015	...	0.015	
1.0	0.16 <sup>f</sup>	0.10	+	0.007	0.004	+	0.03	0.005	...	0.006	
$(\text{C}_4\text{H}_6)/(\text{N}) = 0.25$											
10.4	3.6 <sup>g</sup>	0.35	+	0.010	0.009	0.002	0.010	0.004	0.014	0.036	
8.2	1.5 <sup>b</sup>	0.33	0.001	0.014	0.012	0.001	0.026	0.009	0.038	0.022	
7.2	3.2 <sup>c</sup>	0.31	0.001	0.011	0.010	0.001	0.022	0.007	0.033	0.015	
7.2	2.4 <sup>c</sup>	0.33	0.001	0.011	0.010	0.001	0.022	0.007	0.032	0.015	
4.1	1.5 <sup>b</sup>	0.25	0.002	0.007	0.007	0.0005	0.022	0.007	0.034	0.017	
$(\text{C}_4\text{H}_6)/(\text{N}) = 0.12$											
10.4	3.6 <sup>g</sup>	0.19	0.001	0.001	0.001	0.0005	+	+	0.003	0.017	
8.2	1.5 <sup>b</sup>	0.22	0.001	0.002	0.004	0.0005	0.002	0.006	0.016	0.014	
7.2	3.2 <sup>c</sup>	0.18	0.001	0.003	0.003	0.0005	0.003	0.006	0.010	0.011	
7.2	2.4 <sup>c</sup>	0.21	0.001	0.003	0.004	0.0005	0.003	0.006	0.012	0.011	

<sup>a</sup> Calculated from measured pressure assuming  $T = 300^\circ\text{K}$ ,  $(\text{N}_2) = P_{\text{corr}}/(1.87 \times 10^4)$ . <sup>b</sup> Linear flow rate, 5.3 m sec<sup>-1</sup>. <sup>c</sup> Linear flow rate, 5.9 m sec<sup>-1</sup>. <sup>d</sup> Linear flow rate, 3.2 m sec<sup>-1</sup>. <sup>e</sup> Linear flow rate, 2.5 m sec<sup>-1</sup>. <sup>f</sup> Linear flow rate, 1.6 m sec<sup>-1</sup>. <sup>g</sup> Linear flow rate, 2.2 m sec<sup>-1</sup>. <sup>h</sup> Qualitative detection is designated by +.

**Table III.** Relative Chromatogram Peak Areas<sup>a</sup> of Monomeric Products

Condition	4 <sup>b</sup>	1 <sup>c</sup>	2 <sup>d</sup>	5 <sup>b</sup>	3 <sup>d</sup>	6 <sup>b</sup>
$10^4(\text{N}_2)$ , $M$	1.6	0.5	1.6	1.5	1.6	1.5
$10^7(\text{N})$ , $M$	8.1	27	8	8.1	8	8.1
$(\text{C}_4\text{H}_6)/(\text{N})$	6.7	5	5	1.0	0.8	0.25
Linear flow rate, m sec <sup>-1</sup>	7.5	2.3	7.5	5.7	7.5	5.7
Relative yields, %						
Pyrrole	23	28	26	22	24	29
<i>cis</i> -Crotononitrile	2	3	2	2	2	3
<i>trans</i> -Crotononitrile	10	15	10	9	8	13
<i>cis</i> -1-Cyanobutadiene-1,3	11	9	11	16	10	3
<i>trans</i> -1-Cyanobutadiene-1,3	14	10	12	20	13	21
3-Cyanobutene	12	7	12	12	10	3
<i>cis</i> -C <sub>5</sub> CN	4	3	4	3	4	1
<i>trans</i> -C <sub>5</sub> CN	8	6	9	5	8	2
	84	81	86	89	79	75

<sup>a</sup> Normalized to sum of areas of monomeric peaks, including those for unidentified products. Data for conditions 1-4 are averages of at least three experiments with mean deviations of  $\pm 15\%$ . Single experiments were carried out under conditions 5 and 6. <sup>b</sup> Present work. <sup>c</sup> From ref 3, condensed discharge. <sup>d</sup> From ref 3, microwave supported glow discharge.

the decomposition of butadiene consequent upon its excitation to high vibrational levels. Active nitrogen produced by microwave discharge is known<sup>9,10</sup> to contain significant amounts of vibrationally excited ground state ( $X^1\Sigma_g^+$ )  $\text{N}_2$ . The average vibrational excitation is 6.03 kcal/mole of total  $\text{N}_2$ ,<sup>11</sup> similar to the energy of the  $\nu = 1$  level (6.7 kcal/mole). Morgan and Schiff<sup>11</sup> found that the vibrational relaxation process was very slow, taking place, in the absence of added gases, virtually completely on the walls with

a half-life of 0.08 sec under their conditions which were similar to ours. They also concluded from the kinetics of the heterogeneous decay process that there was very little  $\text{N}_2$  in levels above  $\nu = 1$ . If their conclusions are correct, then accumulation in one butadiene molecule of the energy from, for instance,  $6\text{N}_2(\nu = 1)$ , would be necessary to provide sufficient energy for its endothermic conversion (ignoring additional activation energy) to ethylene and acetylene ( $\Delta H^\circ = 39.4$  kcal/mole). In the present work  $(\text{N}_2)/(\text{C}_4\text{H}_6)$  varied from 25 to 4000 (cf. Table II). If approximately half the  $\text{N}_2$  reaching the reactor was in the  $\nu = 1$  state, the probability of a given molecule of butadiene colliding with

(9) F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, **28**, 510 (1958).

(10) K. Dressler, *ibid.*, **30**, 1621 (1959).

(11) J. E. Morgan and H. I. Schiff, *Can. J. Chem.*, **41**, 903 (1963).

six such molecules before colliding with another molecule of butadiene can be estimated with the aid of the kinetic theory of gases to be between  $(13/15)^6$  and  $(2000/2002)^6$ , *i.e.*, between about 0.4 and 0.94. In order for such a set of six collisions to lead to the decomposition of a butadiene molecule the efficiency of transfer of the vibrational energy of the nitrogen to internal modes of butadiene must be unity. This efficiency is probably, however, very low since butadiene does not absorb significantly in the neighborhood of  $4.28 \mu$ , the wavelength corresponding to 6.7 kcal/mole. It does not seem likely, therefore, that this mechanism of inducing the decomposition of butadiene is important.

Conversion of vibrational energy of  $N_2$  to translational energy, a very inefficient process in active nitrogen itself,<sup>11</sup> might be rendered highly efficient through the mediation of butadiene. If all the vibrational energy of the  $N_2$  were degraded to heat the gas adiabatically, temperatures of the order of  $1000^\circ$  would be produced, ample for pyrolysis. The gas temperature does not rise above  $60$  or  $70^\circ$ , however, presumably because of efficient energy loss to the walls and thence to the environment. Thus true pyrolysis is probably not an important mode of decomposition of butadiene.

Other mechanisms of excitation of butadiene to dissociative levels are conceivable but very hard to evaluate without additional evidence. These include collisional activation of butadiene by excited products of attack of  $N(^4S)$ , *e.g.*, HCN, transfer to internal modes or electronic excitation of a substantial portion of the 225 kcal/mole when two nitrogen atoms combine in a termolecular collision with butadiene and excitation of the latter to a triplet state upon collision with  $N_2$ -( $A^3\Sigma_u^+$ ),<sup>6</sup> the  $\nu = 1$  state of which lies 142 kcal/mole above the ground state of  $N_2(X^1\Sigma_g^+)$ .

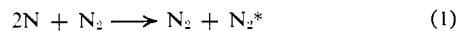
If any of these processes produced butadiene in its first excited singlet state by direct excitation or by system crossing subsequent to primary excitation, decomposition would take place from vibrationally excited ground-state butadiene. This conclusion follows from Srinivasan's study<sup>12</sup> of the photolysis of 1,3-butadiene by which he established that internal conversion of the first excited singlet state precedes decomposition. Comparison of the present results with Srinivasan's data appears to exclude decomposition of vibrationally excited ground-state butadiene as a major mode of formation of degradative hydrocarbons. It should be noted that the relatively low temperature of his experiments renders them more comparable to the work reported herein than are pyrolytic studies<sup>12-14</sup> since secondary thermal processes are minimized. Since neither  $H_2$  nor  $CH_4$  was collected in the present work comparison must be with the other "photolytic" products,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $CH_2=C=CHCH_3$ , and  $HC=CC_2H_5$ , which were produced<sup>12</sup> in the ratio of 1:1.3:1.4:0.6:1.5. Comparison is made most appropriately with the present results with excess butadiene, *i.e.*, with  $(C_4H_6)/(N) = 6.7$ , so as to minimize secondary attack of N on the products. Neither of Srinivasan's  $C_4$  products was identified under these conditions and the ratio of the  $C_2$  products was approx-

imately 1:6:2. With  $(C_4H_6)/(N) = 1.0$ , ethylene and acetylene should be selectively removed by secondary attack of N; yet, under these conditions,  $(C_2H_6):(C_2H_4):(C_2H_2) \cong 1:10:5$ . The most conclusive aspect of the comparison is the contrast between the prominence in the products of reaction with active nitrogen of the  $C_3$  hydrocarbons, propane, propene, allene, and propyne, and their absence from the products of photolysis.

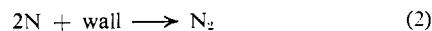
The viewpoint adhered to in the balance of this discussion is that, in the absence of evidence to the contrary, it is assumed that all products originate in the attack of  $N(^4S)$  atoms on butadiene.

**HCN.** The data of Table II establish that, with possibly two exceptions, the fractional conversion of  $N(^4S)$  to HCN at fixed values of the ratio,  $R_R = (C_4H_6)/(N)$ , is constant. The two exceptions, observed at  $R_R = 6.7$  and  $1.0$ , both occur at the lowest concentration of  $N_2$  employed in this work,  $0.16 \times 10^{-4} M$ , corresponding to a pressure of 0.3 torr, and at the lowest concentrations of N and  $C_4H_6$  as well. Under these conditions, (mean free path of  $N_2$  is 0.18 mm) diffusion of N to the wall becomes more important and wall decay of N in the reactor tends to compete more significantly with its collisions with butadiene. If these two data are discarded the mean values of  $R_{HCN} = (HCN)/(N)$  and their standard deviations are  $0.27 \pm 0.014$  at  $R_R = 6.7$ ,  $0.28 \pm 0.016$  at  $R_R = 1.0$ ,  $0.31 \pm 0.019$  at  $R_R = 0.25$ , and  $0.20 \pm 0.011$  at  $R_R = 0.12$ .  $R_{HCN}$  is essentially independent of  $R_R$  except when the latter is very small, *i.e.*, when N is in large excess over  $C_4H_6$ , and even then  $R_{HCN}$  decreases by only about 30%. It is necessary to explain this near constancy of  $R_{HCN}$  first. Fluctuations in its value can be considered as secondary in nature.

The near constancy of  $R_{HCN}$  implies that all significant competing paths of removal of N remain of nearly constant relative importance over the entire range of concentrations employed. The limiting case of this relationship is that only *one* path is significant and this path is characterized by conversion of about 30% of N to HCN. Six possible competing elementary processes which suggest themselves are indicated in eq 1-6 along with corresponding rate laws.

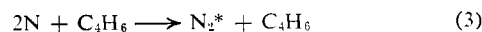


$$-d(N)/dt = k_1(N)^2(N_2) \quad (1a)$$

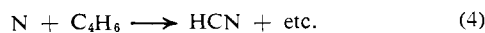


$$-d(N)/dt = k_{2a}(N)/(N_2) \quad (2a)$$

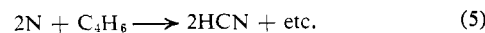
$$-d(N)/dt = k_{2b}(N)^2 \quad (2b)$$



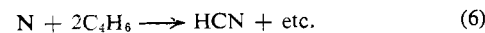
$$-d(N)/dt = k_3(N)^2(C_4H_6) \quad (3a)$$



$$-d(N)/dt = d(HCN)/dt = k_4(N)(C_4H_6) \quad (4a)$$



$$-d(N)/dt = d(HCN)/dt = k_5(N)^2(C_4H_6) \quad (5a)$$



$$-d(N)/dt = d(HCN)/dt = k_6(N)(C_4H_6)^2 \quad (6a)$$

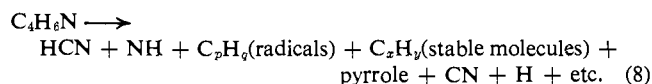
(12) I. Haller and D. R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964).

(13) M. T. Murphy and A. C. Duggan, *J. Am. Chem. Soc.*, **71**, 3347 (1949).

(14) G. M. Badger and T. M. Spotswood, *J. Chem. Soc.*, 4431 (1960).

Equation 2a assumes that diffusion of N to the wall is rate determining while eq 2b assumes that adsorption

equilibrium is maintained.<sup>15</sup> Barring remarkably fortuitous combinations of specific rates, the significant paths for removal of N can be of constant relative importance over the experimental range of concentrations only if they are of identical kinetic order in all relevant species. It has already been suggested that  $R_{\text{HCN}}$  diminishes at sufficiently low ( $\text{N}_2$ ) because the process represented by eq 2a becomes significant. Apparently, at higher pressures it is not. In fact, except for reaction 2a at very low ( $\text{N}_2$ ), reactions 1 and 2 can be discarded because they are of zero order in butadiene while, on the basis of the assumption that all products originate in the attack of  $\text{N}(^4\text{S})$  on butadiene, HCN producing reactions must be of some positive order in substrate. (More than 50-fold variation in ( $\text{C}_4\text{H}_6$ ) at constant ( $\text{N}$ ) and ( $\text{N}_2$ ) causes little change in  $R_{\text{HCN}}$ .) Reactions 3, 5, and 6 can be excluded because they involve processes which are third order over-all in species present at very low concentrations. Even in the unlikely event that such processes took place at rates equal to collision frequencies, it can be estimated that the consumption of N between reactor and trap would be negligible (of the order of 1% under the most favorable circumstances, down to less than 0.01%). This process of elimination leaves only reaction 4, but this reaction (actually a set of reactions), as written, does not appear capable of accounting by itself for the incomplete conversion of N to HCN. This can be accomplished if, as has been suggested previously,<sup>3</sup> reactions 4 are replaced by reactions 7 followed by a set of very rapid unimolecular decompositions (eq 8) the products of some of which undergo further rapid reactions (eq 9).



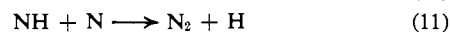
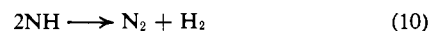
It should be emphasized that  $\text{C}_4\text{H}_6\text{N}$  may not be a single species. One isomer may be the quartet

$\text{CH}_2=\text{CH}=\text{CHCH}_2\text{N}\cdot$  formed in a spin-permitted reaction which is slow compared to reactions 8 because it is of higher order in very dilute reagents. This process probably has a small activation energy also. Possibly, some fraction of  $\text{C}_4\text{H}_6\text{N}$  consists of a doublet or doublets formed in spin forbidden reactions. Equation 9 represents a sum of reactions analogous to 7 and 8 the specific rate of the first step of which would be more rapid than reaction 7 because neither bond breaking nor change in multiplicity is necessarily involved. It has been shown previously that under one set of conditions, about 75% of the fixed nitrogen appears in HCN.<sup>3</sup> The other 25% can be ignored for the time being aside from noting that it must be assumed that its amount relative to HCN remains constant over our range of variables. Presumably,  $\text{NH}$ <sup>16</sup> disappears by reactions 10 and/or 11.<sup>17</sup> According to this scheme the value of

(15) Cf. W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, pp 186, 187.

(16) Cf. P. Goudmand, G. Pannetier, O. Dessaux, and L. Marsigny, *Compt. Rend.*, **256**, 422 (1963), for spectroscopic identification of NH in the emission characteristic of the reactions of active nitrogen with organic compounds.

(17) H. A. Dewhurst and G. D. Cooper, *J. Am. Chem. Soc.*, **82**, 4220 (1960).



$R_{\text{HCN}}$  is essentially determined by the ratios of HCN to NH produced in reaction sets 8 and 9 and should be constant even when  $R_{\text{R}}$  is substantially less than unity. It is possible that the 30% diminution in  $R_{\text{HCN}}$  observed when  $R_{\text{R}} = 0.12$  can be ascribed in part to a significant portion of the HCN being derived from attack of N on stable products (e.g.,  $\text{C}_2\text{H}_4$ ) and the ratio of HCN to NH produced in such attacks being lower than in reaction 8. It seems more likely to be due to a larger proportion of NH disappearing *via* reaction 11. According to this reaction one hydrogen atom can remove two nitrogen atoms. Another possibility is that when  $R_{\text{R}}$  is 0.12, reaction 1 consumes a sufficient fraction of the atomic nitrogen to reduce  $R_{\text{HCN}}$  significantly. That reaction 1 is, even under these conditions, only a minor reaction path follows from the fact that fourfold variation of the product ( $\text{N})^2(\text{N}_2)$  with  $R_{\text{R}} = 0.12$  does not significantly affect  $R_{\text{HCN}}$ .

**Ethane.** The sensitivity of the ethane yield to wall conditions and its small magnitude reduce its quantitative significance. There is some suggestion in the data that  $R_{\text{C}_2\text{H}_6}$  increases as ( $\text{N}_2$ ), *i.e.*, pressure, decreases. This suggestion is consistent with the observed sensitivity to wall conditions. Ethane appears to be formed, at least in part, at the wall. There appears to be relatively little secondary attack on ethane with  $R_{\text{R}} < 1$ . This is consistent with the relatively low reactivity of ethane toward active nitrogen.<sup>18</sup>

**Ethylene.** The principal feature of  $R_{\text{C}_2\text{H}_4}$  is its constancy at given  $R_{\text{R}}$  and its steady diminution with decreasing  $R_{\text{R}}$ . These observations are consistent with the formation of  $\text{C}_2\text{H}_4$  principally in one or more of the set of reactions summarized by eq 8 and its subsequent consumption by reaction 9. The high reactivity of  $\text{C}_2\text{H}_4$  to active nitrogen is well known.<sup>19</sup> There is some indication that  $R_{\text{C}_2\text{H}_4}$  may fall off at very low ( $\text{N}_2$ ), presumably because of the increased importance of reaction 2a.

**Acetylene.** Values of  $R_{\text{C}_2\text{H}_2}$  are more scattered than are the ethylene yields. Within this limitation the pattern is similar to that observed for ethylene except that there is little sensitivity to  $R_{\text{R}}$  other than at its minimum value. Acetylene appears to be formed, like HCN and  $\text{C}_2\text{H}_4$ , in one or more of reactions 8 but to be less reactive than the latter to attack by active nitrogen.

**Propane.** Quantitative data for this product are so few as to limit interpretation severely. Comparison of  $R_{\text{C}_3\text{H}_8}$  with  $R_{\text{C}_2\text{H}_6}$  indicates that propane is not derived from secondary addition of hydrogen to propylene. Perhaps propane is a secondary product but derived from one or more radical (or carbene) products of reactions 8.

**Propylene.** The values of  $R_{\text{C}_3\text{H}_6}$  follow the same pattern as the data for ethylene. Presumably the same interpretations are applicable although the formation of  $\text{C}_2\text{H}_4$  in reactions 8 may seem more plausible than does the formation of  $\text{C}_3\text{H}_6$ . The companion product of the latter would presumably be CN radical. The total yield of products which might be considered to be derived from reaction with cyanogen radical is not known

(18) A. N. Wright and C. A. Winkler, *Can. J. Chem.*, **40**, 1291 (1962).

(19) Cf., e.g., E. M. Levy and C. A. Winkler, *ibid.*, **40**, 686 (1962).

and would at best be very difficult to determine because some nitrile products may be primary products of reactions 8. It is clear from the data of Table II that a substantial portion of the CN dimerizes to cyanogen.

**Allene.** The data for allene are rather badly scattered, probably because of the imperfect separation of this product from propylene. Within this limitation the values of  $R_{\text{allene}}$  fall into a pattern most closely resembling the data for acetylene. Thus allene appears to be relatively unreactive to attack by excess active nitrogen.

**Propyne.** This product is the most abundant hydrocarbon among the degradative products when active nitrogen is in excess. Because it was not separated from recovered butadiene when  $R_R \geq 1$ , there are no data under these conditions. It can only be guessed that it is also a prominent product under the latter conditions. Propyne and allene could both be formed in reactions 8 with HCN and H or CN and  $H_2$  as co-products.

**Cyanogen.** This product is most obviously formulated as arising from dimerization of CN, a species which has been observed spectroscopically in the flames associated with the reactions of a number of organic substrates with active nitrogen.<sup>20</sup> Although  $R_{C_2N_2}$  values are scattered rather badly, it is apparent that there is relatively little systematic variation of this quantity over the entire range of concentrations employed. This observation is consistent with the low rate of destruction of cyanogen by active nitrogen at room temperature.<sup>21</sup> It suggests that all significant processes which consume CN radical are of identical (presumably second) order in CN or in CN plus species whose concentrations are proportional to (CN). This would be true of all reactions of CN with stable or unstable primary products formed in reactions 8. It would not be true of reaction of CN with butadiene. It appears that the latter reaction must be relatively slow so that it does not consume a significant fraction of the cyanogen radical under any of the conditions of Table II. If it is assumed that all of the  $C_4CN$  products reported in Table III arise from the attack of CN on butadiene (and recalling<sup>3</sup> that about 5% of applied  $N(^4S)$  is found in the combined monomeric products), then the amount of CN which forms cyanogen is about twice the amount which is combined in  $C_4CN$  products. The situation is equivocal. Possibly a substantial fraction of the  $C_4CN$  product arises from combination of products of reactions 8, e.g.,  $C_4H_5$  plus CN.

**Monomeric Products.** The data of Table III serve mainly to support our previous report.<sup>3</sup> The only novel result is the finding (in one experiment) that, with N in 4-fold excess over butadiene, the relative yields of  $C_4N$  products are essentially the same as with  $R_R \geq 1$  but that relative yields of all  $C_4CN$  and  $C_5CN$  products except *trans*-1-cyanobutadiene are substantially reduced. These results can be accommodated within the mechanistic framework which was suggested originally<sup>3</sup> and which is elaborated above. In order to do this it must be assumed that products the yields of which are reduced at  $R_R \leq 1$  are formed by the reaction of butadiene with reactive species formed in reactions 8 (cf. reactions 3 of ref 2). *trans*-1-Cyanobutadiene, how-

ever, appears to result from combination of two species, e.g., butadienyl radical and CN, produced in reactions 8. The latter deduction supports the analysis of cyanogen yields given above.

**Other Products.** The lack of detailed data on the dependence of yields of acrylonitrile and acetonitrile on  $R_R$  reduces the basis for mechanistic speculation. Both products could result from attack of CN on unstable or stable products of reactions 8 or by the attack of N on either butadiene or its degradation products. The formation of substantial yields of acrylonitrile over a wide range of values of  $R_R$  tentatively suggests that this product is formed directly in reactions 8.

The frequently observed preponderance of *cis*-2-butene over its more stable *trans* isomer indicates stereospecific synthesis of the former. The apparent absence of 1-butene could be due to either thermodynamic or kinetic control of the reduction process. The formation of *trans*-2-butene in two experiments is currently without explanation. Butane apparently is formed under conditions such that butene can compete with butadiene for hydrogen atoms, i.e., with  $R_R \leq 1$ .

## Experimental Section

Apparatus, materials, and procedures were essentially the same as have been reported<sup>3</sup> except as discussed below. The procedure used in conditioning the reactor wall is described under Results.

**Concentration of N.** The concentration of N at the reactor was controlled by positioning the microwave radiator (Raytheon Type A) either 30, 60, or 90 cm upstream from the reactor inlet and either 2 or 6 cm from the glass surface as well as by varying the power output of the Raytheon Model KV-104(NB) 2450-Mc microwave generator. Flow rates of atomic nitrogen at the various positions and power outputs were determined periodically by nitric oxide emission titration<sup>1</sup> with visual determination of the end point. The afterglow intensity in the reactor was monitored before each run with an Eldorado Electronics Co. Model 200 photometer equipped with a Model 200 C316 detector. Integrated emission intensity measured in this way is *not* a reliable measure of nitrogen atom concentration since the ratio of these quantities changes with time, presumably due to emission at the walls. However it served as a warning of potential changes in the concentration of atomic nitrogen. Irregular changes in the product yields also served this function.

**Concentration of Butadiene.** In order to assure a constant flow rate of butadiene during the brief reaction periods characteristic of this work, butadiene was bypassed around the reactor (E of ref 3) to the vacuum manifold until its rate of flow was constant. The butadiene was then channeled into the reactor to contact the previously established steady flow of active nitrogen.

**Trapping and Transfer of Degradative Products.** Trapping efficiency was improved by replacing traps H and I of ref 3 by units approximately 30 cm long consisting of three concentric tubes, of od 1.8, 3.2, and 5.1 cm, respectively, assembled so as to provide an inner well of refrigerant to supplement that which was applied externally. With traps F, H, and I (cf. ref 3) all cooled by liquid nitrogen, fast flowing ethylene (the most volatile product which was studied) was trapped essentially quantitatively. In experiments devoted to monomeric products trap F was cooled with Dry Ice-trichlorethylene as before.<sup>3</sup>

Reactions were terminated by simultaneously turning off the discharge and closing the stopcock at the butadiene inlet. The nitrogen inlet and the outlet to vacuum were closed immediately thereafter. The products were allowed to vaporize and to expand into the isolated part of the manifold at room temperature. They then were transferred with the aid of a Toepler pump and recondensed at  $-196^\circ$  at G (ref 3) in a W-shaped trap equipped with three stopcocks and partially packed with rolled 20 mesh copper gauze. The trap was allowed to come to room temperature and the degradative products and recovered butadiene were then swept into the gas chromatograph by the stream of helium carrier gas. This procedure assured transfer of the entire product to the gas chroma-

(20) Cf., e.g., K. D. Bayes, *Can. J. Chem.*, **39**, 1074 (1961).

(21) C. Haggart and C. A. Winkler, *ibid.*, **38**, 329 (1960).

tograph. It could be applied to reaction periods of up to 32 min under the conditions employed.

**Analysis of Products.** Routine separations and quantitative determinations were carried out on an F and M Model 500 instrument with an 8 ft  $\times$  0.25 in. od silica gel column, a temperature program covering the range 50–200° at 4° min<sup>-1</sup>, and a helium flow rate of 30 cc min<sup>-1</sup>. A typical chromatograph is shown in Figure 1. Retention times and area factors were determined with authentic samples. Areas were usually estimated by multiplying peak heights by their half-height widths. Separation of the nine products listed in Table II were clean except that propylene and allene overlapped, butane appeared as a tail-like shoulder on the cyanogen peak, and propyne was not completely separated from the single peak due to recovered butadiene plus *cis*-2-butene. These overlaps reduced the precision of determination of allene and propene, prevented quantitative estimation of butane by gas chromatography, and limited the ability to detect and determine propyne gas chromatographically to conditions where relatively little butadiene was recovered.

Acrylonitrile and acetonitrile could not be separated on silica

gel. They could be separated readily on diisodecyl phthalate and relative peak areas were determined on this absorbent. Area factors were not determined. Monomeric products were determined on Carbowax 20M as described previously.<sup>3</sup>

Propene was separated completely from allene and propyne from butadiene, both for purposes of infrared identification, by chromatographing on 8 ft of molecular sieve 5A, programmed from 200 to 250° at 5.6° min<sup>-1</sup>.

A number of the less abundant products were isolated for infrared analysis from the products of runs carried out for several hours. A Perkin-Elmer Model 237 infrared spectrophotometer was used in conjunction with a 7.5-cm gas cell with NaCl windows to identify all products by comparison of spectra with those of authentic samples.

**Materials.** Nitrogen was Matheson "prepurified" grade (99.996%) further purified as described previously.<sup>8</sup> 1,3-Butadiene was Matheson CP, purified by distilling on the vacuum line three times, discarding the first and last tenth each time. Nitric oxide was Matheson 99% purity distilled twice under vacuum at -131.5° (pentane slush).

## Reactions Proceeding by the [3.2.1] Bicyclic Path<sup>1</sup>

Melvin S. Newman and Constantinos Courduvelis<sup>2</sup>

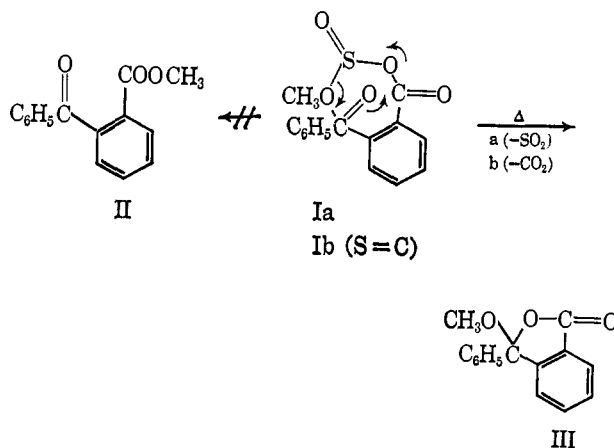
Contribution from the Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210. Received October 8, 1965

**Abstract:** Pyrolysis of intermediates Ia and Ib affords pseudo- ( $\psi$ ) methyl 2-benzoylbenzoate exclusively. Reaction of 2 moles of 2-benzoylbenzoic acid with 1 of ethoxyacetylene yields an intermediate (IX) which affords 2-benzoylbenzoic acid anhydride (X) shown to have the *n, $\psi$*  structure instead of the *n,n* structure previously assigned. Reaction of 1 mole of 2-benzoylbenzoic acid with 1 of ethoxyacetylene yields 1-ethoxyvinyl 2-benzoylbenzoate (XV), which is rearranged to ethyl 3-phenylphthalide-3-acetate (XVI). The acid chloride of 2-benzoylbenzoic acid, however prepared, always has a cyclic structure. All of the above observations can be explained by the use of a [3.2.1] bicyclic path.

Since the discovery of a new reaction path does not occur frequently, the observations which led to the original experiments designed to test the hypothesis are of interest. The rate of alkaline hydrolysis of methyl 6-methyl-2-benzoylbenzoate had been found to be greater than that of methyl 2-benzoylbenzoate<sup>3</sup> and the rate of acid-catalyzed esterification of 6-methyl-2-benzoylbenzoic acid with methanol had been found to be greater than that of 2-benzoylbenzoic acid.<sup>4,5</sup> Both of these results were explained by mechanisms which involved attack of a reagent on the ketonic carbonyl rather than the carbonyl of the carboxy function.<sup>6</sup> Since these reactions are intermolecular, the idea occurred that intramolecular reactions involving attack on the ketonic carbonyl might be discovered if suitable molecules were synthesized.

The first test of this idea involved the formation of an intermediate (Ia) by reaction of sodium 2-benzoylbenzoate with methyl chlorosulfite.<sup>7</sup> On warming, Ia

could yield normal methyl 2-benzoylbenzoate (II) or the pseudo- ( $\psi$ ) ester, III. Although the yield of ester was small (35%) in this experiment *only*  $\psi$  ester was formed. The formation of  $\psi$  ester could be formulated by an intramolecular attack, as shown, and thus a [3.2.1] bicyclic path seemed indicated. This encouraged, other reactions were tried and are described below.



(1) This research was supported by Grant GP-718 from the National Science Foundation.

(2) The material in this paper was taken from the thesis presented by C. C. to The Ohio State University, 1965.

(3) M. S. Newman and S. Hishida, *J. Am. Chem. Soc.*, **84**, 3582 (1962).

(4) M. S. Newman and C. Courduvelis, *ibid.*, **86**, 1893 (1964).

(5) M. S. Newman and C. Courduvelis, *J. Org. Chem.*, **30**, 1795 (1965).

(6) Other examples of such attacks are to be found in the papers of F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962), and of M. L. Bender and M. S. Silver, *ibid.*, **84**, 4589 (1962).

(7) M. S. Newman and W. S. Fones, *ibid.*, **69**, 1046 (1947), showed that sodium salts of acids react with *n*-butyl chlorosulfite to form intermediates which are converted to *n*-butyl esters on heating.