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THE REACTIONS OF ACTIVE NITROGEN WITH ORGANIC MOLECULES

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1. INTRODUCTION

The fixation of nitrogen continues to be the subject of extensive studies in organic chemistry, biochemistry, photochemistry, electrochemistry, and radiation chemistry. This problem is vitally important, and at the same time difficult to solve. Molecular nitrogen is characterised by an unusual chemical inertness, which makes it impossible for nitrogen to react chemically with the great majority of chemical substances under ordinary conditions. The dissociation energy of nitrogen is 225.96 kcal mole^{-1} (at 298°K), the greater part of this energy (~ 125 kcal mole^{-1}) being required for the rupture of the first bond. These values are so large that they generally cannot be compensated by the liberation of energy on formation of new bonds. For example, the energies of the bonds formed by the nitrogen atom with a number of other elements have the following values (kcal mole^{-1})[1]:

N—H	N—C	N—Si	N—O	N—S	N—P	N—Sb	N—F	N—Cl	N—Br
84	195	105	152.3	116	164.9	111	61	62	70

It is clear that most fundamental reactions involving the rupture of the bonds (or even one bond) in the nitrogen molecule cannot take place spontaneously, without preliminary excitation of the molecular nitrogen. This last requirement is not simple either, however, since all the first excitation levels of molecular nitrogen are relatively high. For example, the excitation of molecular nitrogen to the first vibrational level requires an energy quantum of 0.43 eV. Thus this process will take place to a significant extent only at temperatures of the order of several thousand degrees. The energy required for the electronic excitation of N_2 amounts to not less than 6.167 eV, and that required for photochemical excitation is 8.546 eV.[2] The ionisation potential of N_2 is 15.6 eV.[1] Thus electronic excitation of nitrogen is difficult and requires extremely severe conditions. The central problem in the fixation of nitrogen is therefore the conversion of molecular nitrogen into a chemically active state. There are in principle two possibilities: (1) transfer to the nitrogen molecule of sufficient energy to bring about its electronic or vibrational excitation, dissociation, or even ionisation; (2) mild activation of molecular nitrogen; the mechanism of this process has not been elucidated, but it takes place in the fixation of nitrogen in biological systems. The second possibility has led to search for chemical systems providing models of these biological systems, and encouraging results have already been obtained[3-7]. Possible routes to chemical activation of N_2 in these systems have been examined[3,5]. Significant excitation of molecular nitrogen is achieved in the photochemical and radiation-chemical fixation of nitrogen, and also in discharge reactions. Here we are dealing with energy-rich nitrogen species such as atoms, electronically excited molecules, ions, etc. Routes to the fixation of nitrogen by organic molecules by the irradiation of these systems with hard radiation have recently been indicated[8]. In order to understand the mechanism of these complex reactions, it is important to know how the various active nitrogen species react with organic molecules. A considerable amount of factual material on these problems (particularly concerning nitrogen atoms) has accumulated, and we have tried to summarise this material in the present paper. Generally speaking, the reactions of energy-rich nitrogen species with organic molecules lead to the formation of a wide range of products. Since the present paper is concerned with the problem of nitrogen fixation, however, we shall consider here only the nitrogen-containing products of these reactions.

2. REACTIONS OF NITROGEN ATOMS

The reactions of nitrogen atoms with organic molecules will be examined chiefly on the basis of data obtained in the study of active nitrogen, that is nitrogen withdrawn from an electric discharge. The composition of active nitrogen has been the subject of detailed study since its discovery[9]. Up to the present, the following species have been identified, in addition to non-excited nitrogen molecules: $N(^4S)$, $N(^2P)$, $N(^2D)$, vibrationally excited $N_2(X^1\Sigma_g^+)$, $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(C^3\Pi_u)$, and $N_2(a^1\Pi g)$.

The presence of nitrogen atoms in active nitrogen has been proved by a number of direct physical methods. The ultraviolet range of the absorption spectrum of active nitrogen shows the transitions $NI(^4S \rightarrow 2p^4P)$, $(^4S \rightarrow 3s^4P)$, $(2p^32D \rightarrow 3s^2P)$, and $(2p^32P \rightarrow 3s^2P)$[10].

The forbidden $NI(^2P)$ line ($\lambda = 3466$ Å) can be observed in the emission spectrum of active nitrogen at pressures

close to atmospheric [11-13]. The presence of $N(^4S)$ atoms has also been confirmed by the ESR method [14,15]. The presence of excited $N(^2P)$ and $N(^2D)$ nitrogen atoms could not be detected by this method, however (the sensitivity of the method required concentrations of paramagnetic species in active nitrogen of about 1%) [14]. Much information on the composition of active nitrogen has been obtained using mass spectrometers. The presence of both non-excited [16-23] and excited (metastable) $N(^2P)$ and $N(^2D)$ atoms in active nitrogen has been proved by this method [20,21]. The presence of nitrogen atoms in active nitrogen is very effectively demonstrated by adding nitric oxide. With increase in the rate of supply of NO to a stream of active nitrogen, the colour of the latter changes from yellow-orange through blue to greenish white, with a sharp change in colour at the moment when the N atoms are used up completely. The following reactions take place:

$$NO + N \rightarrow N_2 + O\,, \quad (1)$$

$$N + O + M \rightarrow NO\,(B^2\Pi, A^2\Sigma) + M\,, \quad (2)$$

$$NO\,(B^2\Pi, A^2\Sigma) \rightarrow NO\,(X^2\Pi) + h\nu \text{ (pale-blue luminescence)}, \quad (3)$$

$$NO + O \rightarrow NO_2 + h\nu \text{ (greenish-white luminescence)}. \quad (4)$$

Because of the high rate of reaction (1) ($k \simeq 10^{-11}$ cm^3 molecule^{-1} s^{-1}) almost all the N atoms are used up in this reaction even in the presence of a considerable excess of NO. Kistiakowsky and Volpi [24] suggested this reaction for the determination of the concentration of nitrogen atoms in active nitrogen. The correctness of this procedure was subsequently confirmed by a number of workers: (a) by comparison of the concentration of nitrogen atoms determined by titration with nitric oxide with the value found from the decrease in pressure in an abruptly isolated volume containing active nitrogen [25]; (b) by determination of the equivalence point using the ESR method [15]; and (c) by comparison of the heat liberated in the deactivation of the active species on a cobalt surface with the expected value, calculated on the assumption that only the N atoms whose concentration was determined by titration with nitric oxide are removed on the surface [26].

The concentration of nitrogen atoms in active nitrogen depends on the type of discharge used for the excitation. The active nitrogen withdrawn from a microwave or ultrahigh frequency discharge contains ~ 1% of nitrogen atoms, whereas that withdrawn from a condensed discharge contains up to 100% of nitrogen atoms [27]. Most of the atoms are in the ground (^4S) state. Estimation of the relative concentrations of nitrogen atoms in various excitation states, carried out by spectroscopic [10] and mass-spectrometric [20,21] methods, gave results showing satisfactory agreement and indicated that the concentration of $N(^4S)$ is greater than the concentration of $N(^2P)$ and $N(^2D)$ by 2-3 orders of magnitude. These data relate to the composition of active nitrogen about 1×10^{-3} s after it has left the discharge tube. At later stages of the afterglow, metastable nitrogen atoms cannot be detected at all [20,21]. This is apparently due to the rapid deactivation of the excited atoms on the walls.

Vibrationally excited nitrogen molecules in the ground electronic state ($X^1\Sigma_g^+$) have been observed in active nitrogen by spectroscopic methods. Dressler [28] recorded in the absorption spectrum nine bands from the Lyman-Birge-Hopfield (L-B-H) system ranging from (0,0) to (0,8). In a number of studies of the absorption spectra of the so-called pink afterglow of active nitrogen which lasts about 1×10^{-3} s, it was shown that this nitrogen contains a large quantity of $N_2(X^1\Sigma_g^+)$, excited to high vibrational levels (up to $v = 29$) [29,32]. On the basis of an analysis of ionisation curves for N_2^+, obtained by the mass-spectrometric method, Foner and Hudson [20,21,33] concluded that in the early stages active nitrogen contains $N_2(X^1\Sigma_g^+)$ molecules, whose vibrational energy reaches 7.5 eV. Kaufman and Kelso [34] detected appreciable liberation of heat when N_2O and CO_2 were added to active nitrogen; this can be interpreted as transfer of the vibrational energy of the nitrogen molecules to translational degrees of freedom, sensitised by these additives. According to their estimate, the heat liberated amounted to ~ 2 kcal mole^{-1}, which corresponded to a vibrational energy distribution with 30% of the $N_2(X^1\Sigma_g^+)$ molecules in the vibrational level with $v = 1$. Thermochemical studies of the deactivation of active nitrogen on the surface of a cobalt catalyst confirmed the existence, in active nitrogen, of a large quantity of nitrogen molecules excited to the first vibrational level [26]. It is now assumed that the active nitrogen with which chemical reactions are usually carried out (~ 0.1 s after removal from the discharge tube) does not contain the highly excited vibrational states of $N_2(X^1\Sigma_g^+)$ molecules [35]. As with metastable nitrogen atoms, this is apparently due to the fact that N_2 molecules excited to high vibrational levels are formed only in the discharge, and before they are observed in the chemical reaction vessel they are able to redistribute their energy in collisions with non-excited nitrogen molecules. For example, 1×10^{-4} s after leaving the discharge, active nitrogen contains $N_2(X^1\Sigma_g^+)$ molecules with vibrational energy up to 7.5 eV; [33] the corresponding figures after 1×10^{-3} s and 1×10^{-2} s are 7.16 eV [29-32] and 2.36 eV [28] respectively, and after 5×10^{-2} s active nitrogen contains only N_2 in the first vibrational level ($E_{v=1}$ = 0.43 eV) [26]. Estimates of the concentrations of vibrationally-excited nitrogen molecules, carried out in the early stages of the afterglow, give values which showed good agreement: 10% according to the absorption spectra [28,29] and 8% from mass-spectrometric data [33]. Study of the deactivation of vibrationally-excited nitrogen molecules in the later stages of the afterglow with the aid of N_2O has given estimated values for the concentration of $N_2(X^1\Sigma_g^+$, $v = 1$) of 30% [34] and more [26].

The intense emission by bands of the first positive system of nitrogen ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) suggests that active nitrogen contains considerable concentrations of metastable $N_2(A^3\Sigma_u^+)$ molecules, since the radiative lifetime of this state, according to recent estimates, is of the order of 10 s, and its deactivation by collision with N_2 is hindered [13,36]. Nevertheless, optical transitions from this state in active nitrogen (pressure about 1 mmHg) have not been observed, either in the absorption spectra under ordinary conditions [37] or in the emission spectra [Vegard-Kaplan bands (V-K bands)] [35,38-40]. Corresponding transitions were observed in the discharge [41,42], and its was established that, in order to observe the V-K bands, it is necessary to have very pure nitrogen; traces of Hg and O_2 are particularly harmful [32]. It may be assumed that the $N_2(A^3\Sigma_u^+)$ molecules in active nitrogen are rapidly deactivated in collisions with the walls or impurities. Working with pure nitrogen, Noxon [11,13] observed fairly intense luminescence of V-K bands in active nitrogen at high pressure (up to 1 atm), when deactivation on the walls was hindered. After thorough purification of nitrogen, Zipf [36] was also able to observe V-K bands in the afterglow of nitrogen in the pressure range 0.1-10 mmHg. Young [40] concluded that nitrogen atoms can play the same role as an impurity in the deactivation of $N_2(A^3\Sigma_u^+)$ molecules. On collision, exchange by atoms takes place according to the reaction:

$$N + N_2(A^3\Sigma_u^+, v=0) \rightarrow N_2(X^1\Sigma, v=25) + N\,. \quad (5)$$

According to his estimates, this reaction takes place very rapidly ($k = 2 \times 10^{-10}$ cm^3 s^{-1}). This might have explained the decrease in the intensity of the V–K bands with increase in the concentration of nitrogen atoms [13,36]. If Young is correct, however, it is difficult to understand why $N_2(X^1\Sigma_g^+)$ molecules, excited to high vibrational levels, cannot be detected in the afterglow after 5×10^{-2} s. The greater intensity of the V–K bands compared with the first positive system of nitrogen, observed by Noxon and Zipf, suggests that there exist other sources of $N_2(A^3\Sigma_u^+)$ molecules in addition to recombination of atoms. One such source is undoubtedly the discharge. This is indicated by the results of mass-spectrometric studies [20,33], in which it was established that $N_2(A^3\Sigma_u^+)$ molecules are present in active nitrogen in significant concentrations only 100 μs after leaving the discharge (100 μs was the lower limit in these experiments) and are observed throughout the entire time interval studied (up to 2×10^{-3} s). It is possible that $N_2(A^3\Sigma_u^+)$ molecules were detected in active nitrogen by the ESR method [43]: the authors cited observed the ESR spectrum of paramagnetic species but the spectrum could not be assigned to nitrogen atoms or free electrons. The rate of deactivation of these species was described by a first-order kinetic equation with a half-life of 0.07 s at a pressure of 4.4 mmHg.

The presence of $N_2(B^3\Pi_g)$ in active nitrogen is evident, since the long-lived yellow afterglow, characteristic of active nitrogen, consists of first positive bands of nitrogen. The bands with $v' > 12$ are usually not observed, but it is possible to observe the band ($B^3\Pi_g$, $v' = 26 \rightarrow A^3\Sigma_u^+$, $v = 20$) by immersing the tube in liquid nitrogen [44]. The Y system ($^3\Sigma_u^- \leftarrow B^3\Pi_g$) has also been observed in the emission spectra at low temperatures [45]. The concentration of $N_2(B^3\Pi_g)$ in active nitrogen should be low, since the emission lifetime of this state is small, of the order of 10^{-6} s. [46]

The second positive system of nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_g$), which proves the presence of electronically excited $N_2(C^3\Pi_u)$ molecules in active nitrogen, can be observed only in the early stages of the afterglow, and its intensity is very low [30]. In this instance $N_2(C^3\Pi_u)$ is apparently formed in the discharge. The authors cited consider that formation of these molecules in the afterglow by $N(^4S) + N(^2D)$ collisions was observed when active nitrogen was cooled to liquid nitrogen temperature [47].

The emission of L–B–H bands ($a^1\Pi_g \rightarrow X^1\Sigma_g^+$), whose intensity is much less than that of the first positive system, was observed in the far ultraviolet [10]. Thus $N_2(a^1\Pi_g)$ molecules are present in active nitrogen in very small quantities. Mass-spectrometric methods have confirmed that active nitrogen contains highly excited electronic states of molecular nitrogen (probably $a^1\Pi_g$ or $a'^1\Sigma_u^-$, with energies of 8.548 eV and 8.398 eV respectively), but these states could be observed in quantities comparable with the concentrations of $N_2(A^3\Sigma_u^+)$ only within time intervals less than 1×10^{-3} s after the active nitrogen had left the discharge [20,33].

The presence of excited molecules in active nitrogen is revealed chemically: (1) in the decomposition of NH_3 [22,35,48–59] (nitrogen atoms doe not react with NH_3 [52,55]); (2) in the decomposition of nitric oxide to an extent greater than that corresponding to reaction (1) [51,60]; and (3) in the existence of a low-temperature (< 150°C) mechanism of the reaction of hydrocarbons with active nitrogen, differing from the high-temperature mechanism (> 150°C) [57,59]. The states of the excited nitrogen molecules responsible for these effects have not yet been identified. It has merely been established that NH_3 and hydrocarbons apparently react with the same excited nitrogen molecules, since the addition of NH_3 decreases the yield of HCN in the reaction of active nitrogen with hydrocarbons [57]. It has also been shown that NH_3 and NO react with N_2^* species in different excited states, since competition between them is not observed in their reaction with active nitrogen [51]. Herron [22] confirmed this conclusion and showed that NH_3 reacts with electronically excited metastable N_2 molecules, which can be observed by mass-spectrometric methods. Since the emission lifetime of the N_2^* species reacting with NH_3 is large (apparently much greater than 0.1 s [35,51,56]), it may be assumed that these are $N_2(A^3\Sigma_u^+)$ molecules.

To summarise, it may be concluded that active nitrogen, 0.1 s after its removal from the discharge, contains appreciable quantities of $N(^4S)$ atoms and vibrationally-excited $N_2(X^1\Sigma_g^+, v = 1)$ molecules, together with a small quantity of electronically-excited molecules, apparently in the $A^3\Sigma_u^+$ state. It is usually this active nitrogen which is used to study its chemical reactions with organic molecules. It has now been established that atomic nitrogen is the chief chemical reagent in active nitrogen [51,61–63].

The reactions of active nitrogen with organic molecules have now been studied for a long time, beginning with the work of Strutt (1911). The general features of the procedures used in these studies can be described as follows. Active nitrogen is prepared in a discharge at a nitrogen pressure of several mmHg, produced in a discharge tube by various methods. A condensed discharge, microwave discharge, or ultrahigh frequency discharge is usually employed. At atmospheric pressure active nitrogen is obtained by means of ozonisers. A current of nitrogen activated in this way is withdrawn from the discharge tube and passed into the reaction vessel. The organic compound is introduced into the same reaction vessel and reacts with the active nitrogen. The products formed are frozen out in traps and studied by chemical and physicochemical methods. The most extensive studies of the reactions of active nitrogen with organic molecules have been carried out by Winkler and coworkers. In 1956 they summarised the result of approximately ten years of work in this field [63]. The main conclusions can be summarised as follows: in the majority of reactions of active nitrogen with saturated and unsaturated hydrocarbons, alkyl chlorides, alkyl cyanides, and alkylamines, the chief and sometimes the only nitrogen-containing product is HCN; a characteristic feature of the reaction with unsaturated hydrocarbons is the formation of a nitrogen-containing polymer and a small quantity of C_2N_2; under certain conditions, all the N atoms are used up in reactions with the organic molecules. The range of studies of the chemical reactions of organic compounds with active nitrogen has now broadened considerably. A number of qualitatively new results have been obtained (some of these have been examined in a review by Mannella [64]); the most important of these results is the production of new nitrogen-containing compounds—NH_3 and various nitriles—in appreciable yield. Table 1 gives all the organic compounds whose reactions with active nitrogen have been studied, together with the reaction products. The plus sign indicates the products observed in the reaction between active nitrogen and the organic molecules listed on the left-hand side of the Table. As before, a common feature of these reactions is the formation of HCN, usually in highest yield. The preferential formation of CH_3CN in the reaction of active nitrogen with propene, observed by Lichtin [65], has not yet been confirmed [66]. Other charac-

teristic products are cyanogen and a nitrogen-containing polymer. Here, to supplement the earlier summary[63], it may be noted that the formation of a nitrogen-containing polymer and a certain amount of cyanogen is characteristic not only of unsaturated compounds, but also of halogenated hydrocarbons. The formation of a solid polymer is often observed with other organic compounds. Up to 65% of the nitrogen reacting goes into this deposit, depending on the specific system. The composition of the deposit depends on the nature of the organic compound reacting with active nitrogen: the concentration of nitrogen in the deposits obtained by various workers[77,78,82,84,87,96] varied from 16% to 37%. The polymer formed in the reaction with acetylene has been shown to have a formula of the type[90]:

$$-\underset{\underset{CN}{|}}{CH}-(CH=CH)_n-\underset{\underset{CN}{|}}{CH}-$$

In the reaction with buta-1,3-diene, the deposit has the formula $(C_4H_6N)_x$,[84] and the reaction with isoprene gives the polymer $(C_3H_5N)_x$.[88] The deposit formed in the reactions with halogen-substituted hydrocarbons contains the halogen[99], and the products of the reactions with silanes have been found to contain Si–N and Si–C bonds[75]. Some experimental results indicate that the deposit is not an individual chemical compound, but a mixture[84,88,97]. Aronovich and Mikhailov[77,78] reported that the nitrogen in the deposit which they obtained is almost completely hydrolysed to NH_3. The ease of hydrolysis suggested to them that the deposit contained nitrile or even imino-groups. The chemical inertness of these deposits makes their study difficult.

TABLE 1. Nitrogen-containing products of the reactions of atomic nitrogen with organic compounds*.

Original organic compounds	Nitrogen-containing products of the reactions: HCN	$(CN)_2$	nitrogen-containing polymer	NH_3	ClCN	CH_3CN	C_2H_5CN	References
Methane	+			+		+		57,66–69
Ethane	+		+	+				51,57,59,63, 66,67,70
Propane	+							59,63,72
Cyclopropane	+							63,73
n-Butane	+			+				51,63,74
Isobutane	+							63,74
Cyclobutane	+							63
Neopentane	+			+				59,67,73,75, 76
Cyclopentane	+							73
n-Hexane	+		+	+				75,77,78
Cyclohexane	+		+	+				75,77,78
n-Hexadecane	+	+		+		+		79
Ethylene	+	+	+	+				23,51,63,69, 70,71,80,81
Propene	+	+	+			+	+	63,65,71,82
But-1-ene	+							63,83
But-2-ene	+			+				51,63,83
2-Methylpropene	+							63,83
Buta-1,3-diene	+	+	+			+	+	84,86
Isoprene	+		+	+				85,87,88
Cyclohexene	+		+					77,78
Benzene	+		+	+				75,77,78
Benzonitrile	+		+					87
Naphthalene	+		+					77,78
Tetralin	+		+					87
Acetylene	+	+	+					63,70,71, 90–94
Methylacetylene	+	+	+					71,92–94
Dimethylacetylene	+	+						92
Diphenylacetylene	+		+					87
Methanol	+					+		68,95
Ethanol	+					+	+	68,96
Propan-2-ol	+							96
Benzaldehyde	+		+					77,78
Cyclohexanone	+		+					77,78
Acetic acid	+		+					77,78
Stearic acid	+		+					77,78
Oleic acid	+		+					77,78
Butyl oleate	+		+					77,78
Dibutyl phthalate	+		+					77,78
Carbon tetrachloride			+		+			89,97,98
Chloroform	+	+	+		+			97,98
Methylene chloride	+	+	+		+			97
Methyl chloride	+	+	+		+			98,99
Methyl bromide	+		+					98
Chloroethane	+	+	+					99
1-Chloropropane	+	+	+					99
2-Chloropropane	+	+	+					99
Chloroethylene	+	+	+					99

TABLE 1 (contd.)

Original organic compounds	Nitrogen-containing products of the reactions: HCN	$(CN)_2$	nitrogen containing polymer	NH_3	ClCN	CH_3CN	C_2H_5CN	References
Methylsilane	+			+				100
Dimethylsilane	+			+				100
Trimethylsilane	+			+				100
Tetramethylsilane	+		+	+				75,100
Siloxane heptamer	+			+				79
Polyethylene	+	+						101
Polypropylene	+	+		+				101
Poly-2-methylpropene	+	+		+				101
Methyl cyanide	+							92–94
Azomethane	+							102
Methylamine	+			+				75,92–94
Ethylamine	+			+				75

* The following products have also been found in reactions of atomic nitrogen: with buta-1,3-diene—1-cyanobuta-1,3-diene, 3-cyanobutadiene, 3-cyanobut-1-ene, 1-cyanopent-3-ene, crotonitrile, and pyrrole; with isoprene—crotonitrile, pyrrole, and β-methylpyrrole; with benzene—benzonitrile, phenyl isocyanide, and pyridine; with naphthalene—quinoline and isoquinoline; and with cyclohexanone—cyanohydrins.

It can be seen from Table 1 that there are a large number of compounds which react with active nitrogen to give ammonia and nitriles; the formation of NH_3 is characteristic of alkanes, methyl-substituted silanes, and polymers containing methyl groups, and the formation of nitriles is characteristic of alkenes and halogenated methanes. A distinctive feature of the reactions of the latter is the formation of ClCN. Ammonia is extremely convenient both for direct use and for subsequent conversion into valuable nitrogen-containing products, so that its formation in the reactions of active nitrogen with organic compounds is of particular interest. Unfortunately, the absolute yield of NH_3 is generally low: for hydrocarbons[70] and siloxane[79], it does not exceed 10 mole %, calculated on the organic reagent decomposed. The yield of NH_3 for methylsilanes is much greater, but the reaction rate is smaller by one order of magnitude than that for hydrocarbons[75]. In all instances the yield of NH_3 is lower than the yield of HCN. The appropriate data (Table 2) show that in the reactions of active nitrogen with hydrocarbons, the yield of NH_3 is usually 10–20% of the yield of HCN. Winkler and coworkers[57] showed, however, that this figure can be increased to 50% by increasing the flow rate of the organic reagent. It should be noted that the latter reaction was carried out below 150°C. There are thus grounds for assuming that excited nitrogen molecules play an important part in altering the mode of the reaction. For organosilicon compounds, a change in the NH_3/HCN ratio with change in temperature was not observed[79,100]. The

TABLE 2. Maximal values of the relative yield of NH_3 obtained in reactions of organic compounds with active nitrogen.

Organic compound	NH_3/HCN, %	References	Organic compound	NH_3/HCN, %	References
Methane	50	57	Methylsilane	2	100
Ethane	16—20	51,70	Dimethylsilane	20—30	100
	50	57	Trimethylsilane	30—40	100
Butane	16	96	Tetramethylsilane	40—50	75,100
Neopentane	20	75	Siloxane heptamer	48	79
Hexane	20	75	Polypropylene	46	101
Cyclohexane	12	75	Poly-2-methylpropene	21	101
n-Hexadecane	10	79	Ethylamine	65	75
Ethylene	15	51,70	Methylamine	89	75
But-2-ene	16	51			
Benzene	18	75			

absolute and relative yields of NH_3 increase with increase in the concentration of methyl groups in the original molecule [88,100,101].

Despite extensive study of the reactions of active nitrogen with organic compounds, few results have indicated the possibility of forming products corresponding to the mild degradation of the original organic molecules in appreciable yield in these reactions. It is these data, however, which throw light on the mechanism of the reaction of active nitrogen with organic molecules. The formation of benzonitrile [77,78,87] and pyridine [77,78] in the reaction of active nitrogen with benzene, and the formation of quinoline and isoquinoline in the reaction with naphthalene [77,78] are of interest in this connection. Work by Lichtin and coworkers [84-86], specially undertaken to find conditions for obtaining products of the mild degradation of the original molecules, showed that a large number of nitriles and pyrrole are formed in the reactions of buta-1,3-diene and isoprene with active nitrogen.

The reactions of active nitrogen with organic molecules are usually very rapid. The kinetic characteristics of a number of reactions are given in Table 3. Most of the kinetic data relate to the overall reactions of HCN formation. In some instances it has been assumed [23,58,95,103,105] that the initial attack by the N atom on the organic molecule is the rate-determining step in the complex reaction of HCN formation, and the kinetic constants obtained by the authors cited relate to the corresponding fundamental reaction. This assumption is based on the view that the subsequent stages leading to the formation of HCN involve organic radicals, and therefore should take place very rapidly. The problem of assigning the experimentally determined effective rate constants to given fundamental reactions can be resolved, however, only after the complete reaction mechanism has been established. Such studies have not yet been carried out for any reaction of active nitrogen with an organic molecule. In the reactions studied the systems always contain atomic hydrogen [23,63], which produces radicals by reacting with the organic molecules; from the kinetic viewpoint this may lead to appreciable "masking" of the initial step in the formation of HCN from atomic nitrogen and the organic molecule. Most kinetic studies of the reactions of active nitrogen with organic molecules have been carried out in low-pressure flow systems. The dependence of the yield of HCN on the concentration of the reagents and temperature, or on the duration of the reaction and temperature, has been studied. The results have been analysed on the assumption that the

TABLE 3. Kinetic constants for the reactions of active nitrogen with various organic molecules*.

Organic molecule	Temperature, °K	A, $cm^3 mole^{-1} s^{-1}$	P		E, kcal $mole^{-1}$		k, $cm^3 mole^{-1} s^{-1}$	Refs.
			laminar	turbulent	laminar	turbulent		
Methane	313—773		10^{-2}—10^{-3}		11—13			63,66,67
Ethane	380—500		3×10^{-3}	7×10^{-2}	6.2	7.9		63,66,67
	423—748		6.4×10^{-4}	2×10^{-3}	5.7	6.3		63,65
	173—423		1.4×10^{-5}	1.2×10^{-5}	2.7	2.4		63,65
	278—423	8.7×10^{-15}	2×10^{-5}		1.7			59
	423—703	3.8×10^{-12}	6×10^{-3}		7			59
Propane	278—703	8.7×10^{-12}	1.9×10^{-2}		5.5			59
	336—523		9.1×10^{-4}	2.1×10^{-2}	5.1	6.2		63,72
Butane	75—250		4.5×10^{-4}		3.6			63,74
Isobutane	100—260		4.4×10^{-4}		3.1			63,67
Neopentane	233—423		1.1×10^{-6}	3.3×10^{-5}	2.0	2.0		63,67
	423—623		2.7×10^{-4}	4.9×10^{-2}	6.5	7.7		63,67
	278—423	4.8×10^{-15}	1.0×10^{-5}		1.5			59
	423—703	2.3×10^{-12}	3.4×10^{-3}		6.6			59
Cyclopropane	—		1.9×10^{-5}	5×10^{-4}	3.2	4.0		63
Cyclobutane	—		1.5×10^{-4}	4.1×10^{-2}	4.6	6.4		63
Ethylene	310		10^{-5}				1.6×10^{-13}	
	295—673		10^{-5}		0.4±0.2		1.7×10^{-14} at I=295°K	103, 104
	473—603				<1		9.6×10^{-14} at I=500°K	105
	320				>1		1.2×10^{-14}	
	291—523	$1.2\times10^{-14}\sqrt{T}$			1.5±0.2		2×10^{-14} at I=320°K	23, 80
	325						6.6×10^{-14}	
	423						3×10^{-14}	81
Acetylene	70—90				0.25			58
	291—523	$9.35\times10^{-16}\sqrt{T}$			2.3±0.2			90
Polyethylene	312—419				1.7±0.7			91, 101
Methanol	303—755		2.3×10^{-3}	3.7×10^{-3}	3.4	3.7		
Ethanol	300—593		3.6×10^{-3}		3.4			95
Propan-2-ol	300—593		3.8×10^{-3}		3.5			96
Azomethane	323—673		10^{-2}—10^{-4}		1.9±0.3			96
Methyl radical	323—673		10^{-1}—10^{-3}		0.5±0.4			102
								102

* Symbols used in the table: A is the pre-exponential term in the expression for the reaction rate constant $k = A\exp(-E/RT)$, P the steric factor, E the activation energy, and k the reaction rate constant.

only chemically active species in the active nitrogen are nitrogen atoms, and that their reactions with organic molecules are bimolecular. For comparatively slow reactions, the calculations of the kinetic constants in a number of instances were carried out assuming both laminar flow and turbulent flow of active nitrogen in the reaction vessel. The methods generally used to determine the concentration of nitrogen atoms are as follows: (a) titration of the stream of active nitrogen with nitric oxide, based on reaction (1); and (b) determination of the maximal yield of HCN in the reaction of active nitrogen with ethylene. The values obtained for the concentration of nitrogen atoms by the first method are on the average one and a half times those obtained by the second method. Until recently it was not clear which method ought to be given preference, so that both were used. Only recently it was shown convincingly [23] that the reaction with ethylene involves recombination of nitrogen atoms, catalysed by intermediate products, so that preference must be given to the reaction with nitric oxide. The kinetic constants obtained by using NO to determine the concentration of nitrogen atoms can therefore be regarded as more reliable.

A second serious source of errors lies in the determination of the reaction time. It is necessary to be able to stop the reaction sharply at a given moment of time, and this is a difficult task in reactions of active nitrogen with organic molecules, particularly reactions with unsaturated compounds, which take place extremely rapidly. Comparison of a number of methods [104] has shown that two are most suitable for this purpose: (1) a method based on the introduction into the reaction zone of NO, which stops the reaction by reacting rapidly with the remaining nitrogen atoms; and (2) the removal of nitrogen atoms from the reaction by rapid surface recombination on a cobalt catalyst. The mean values of the reaction rate constants obtained using the two methods show good agreement [104].

There are a number of other sources of systematic errors in the flow method for studying the kinetics of the reactions of active nitrogen with organic molecules. For example, allowance is not always made for the following factors: deactivation of N atoms within and on the surface of the reaction vessel (flow tube), the influence of the reaction on the pressure gradient in the flow tube and on the rate of flow, the influence of impurities formed by erosion of the electrodes in the discharge tube, and the influence of hydrogen atoms. Thus the kinetic constants obtained in early work must be regarded merely as estimates of the appropriate quantities, to within one order of magnitude. It must also be borne in mind that the data given in Table 3 are influenced by errors associated with imprecise knowledge of the reaction mechanisms. To estimate the magnitude of these errors, it may be noted that the individual values of the rate constants for the reactions of active nitrogen, determined using improved methods, deviate from their arithmetic mean by 10–25% within the ranges of reagent concentration and duration of reaction studied. A regular increase in the rate constants with decrease in the duration of the reaction is observed, indicating the complexity of the process and hence the relative value of the arithmetic-mean rate constants for the reaction of active nitrogen. The reactions of active nitrogen with ethylene have been the subject of the greatest number of kinetic studies, because of the unique part played by this reaction in the study of active nitrogen. The method of diffusion flames [81,103] has been used to obtain approximate values of the rate constant for this reaction. More reliable values were obtained in work [23,104] in which the results were analysed by various methods, and the values obtained for the constants showed good agreement. The most reliable value of the rate constant for the first fundamental step in the reaction of active nitrogen with ethylene,

$$N + C_2H_4 \rightarrow HCN + CH_3 . \qquad (6)$$

is that obtained by Herron [23]. This determination was based on a precise knowledge of the reaction mechanism. Other rate constants [80,100] assigned to stage (6) are slightly higher than those given by Herron. These constants [80,100] apparently cannot be assigned to this fundamental reaction step, and they should rather be regarded as more accurate values of the rate constant for the overall reaction of HCN formation.

The mechanism of the reaction of active nitrogen with organic molecules has not yet been elucidated. In accordance with the unified mechanism proposed by Winkler for these reactions, it is assumed that the nitrogen atoms attack directly one of the carbon atoms in the organic molecule, and that the resulting complex decomposes according to a unimolecular law with the formation of HCN as the product of the primary stage of the reaction, together with organic radicals, which subsequently react rapidly with atoms, again with the formation of HCN. For example, the formation of HCN from propane, propene, propyl chloride, and ethanol can be represented as follows:

$$N + C_3H_8 \rightarrow [NC_3H_8] + H_2 \rightarrow HCN + C_2H_5 + H_2 \qquad (7)$$

$$N + C_3H_6 \rightarrow [NC_3H_6] \rightarrow HCN + C_2H_5 \qquad (8)$$

$$N + C_3H_7Cl \rightarrow [NC_3H_6] + HCl \rightarrow HCN + C_2H_5 + HCl \qquad (9)$$

$$N + C_2H_5OH \rightarrow [NC_2H_5] + OH \rightarrow HCN + CH_3 + OH . \qquad (10)$$

Winkler's mechanism provides a satisfactory explanation for the formation of not only HCN but also new hydrocarbons and other compounds which do not contain nitrogen. In the selection of probable reactions it is necessary only to make allowance for energy and spin restrictions [63]. For reasons related to the energetics of the process, however, it is doubtful if this mechanism is applicable to the reactions of lower hydrocarbons. It has also been shown that that hydrocarbon radicals play an important part in the reactions of hydrocarbons with active nitrogen [106]. Safraniy et al. [106] consider that the lower alkanes must first form radicals, which then react rapidly with N atoms to form HCN. The initial formation of radicals from alkanes is an unresolved problem. It is possible that the excited nitrogen molecules which are present in active nitrogen may act as initiators in these reactions. All that has been said above relates to the mechanism of HCN formation. The formation of NH_3 and the various products obtained by mild degradation of the organic molecules also requires explanation. For example, the pyrrole and *trans*-crotonitrile obtained by the reaction of active nitrogen with buta-1,3-diene can be regarded as the products of the attachment of an N atom to the original molecule and the removal of an H atom. The mechanism of this substitution is not yet clear. Ammonia may be formed by the reactions of N atoms with molecular or atomic hydrogen, produced by the decomposition of the organic reagents with active nitrogen. This was used, in particular, to explain the formation of NH_3 in the reactions of active nitrogen with ethane and ethylene frozen at −196°C. [70] In general, however, this explanation cannot be regarded as satisfactory, as there are a number of serious objections. The formation of NH_3 in a reaction with atomic hydrogen should pass through a stage involving the formation of an NH radical, which decomposes very readily:

$$NH + NH \rightarrow N_2 + H_2 \qquad (11)$$

$$NH + N \rightarrow N_2 + H . \qquad (12)$$

The NH_2 radical, which is the intermediate species in the formation of NH_3 by the reaction of atomic nitrogen with molecular hydrogen, decomposes in analogous fashion:

$$NH_2 + N \rightarrow N_2 + H_2 . \qquad (13)$$

Thus the intermediate species produced in the formation of ammonia not only disappear themselves in side reactions which take place readily, but also lead to the irreversible removal of the original reagent—N atoms—from the reaction. The decomposition of NH and NH_2 radicals should evidently be particularly efficient in an excess of nitrogen atoms, and this is usually the situation in the reactions of active nitrogen with organic compounds. Moreover, the reaction of N with H_2 is termolecular [107]:

$$N + H_2 + N_2 \rightarrow NH_2 + N_2 \qquad (14)$$

and its rate is therefore low ($k = 0.85 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}). It can be observed only at pressures of molecular nitrogen greater than 6 mmHg. [107] The formation of NH_3 is always observed, however, at pressures below

6 mmHg. Thus the formation of NH_3 under the conditions of the reactions of active nitrogen with organic molecules apparently does not take place in secondary reactions of the N atoms with hydrogen liberated by the decomposition of the original organic molecules. The correlation between the formation of NH_3 and the number of methyl groups in the original organic molecule suggests that NH_3 is formed in a single stage in some process in which the N atom displaces two or three H atoms from the CH_3 group[75,89,100].

The reactions of hot N atoms, formed in the process $^{12}C(d, n)^{13}N$, with organic molecules also leads to the formation of chiefly HCN with a small quantity of nitriles[68,69,89,98]. Thermalisation of the ^{13}N atoms does not alter significantly the composition and yield of the products[69]. As in the reactions of active nitrogen, CN radicals do not play a significant part in the formation of the products[69]. Thus the reactions of hot N atoms with organic molecules resemble the reactions of active nitrogen. The mechanism of these reactions is identified with Winkler's unified mechanism, which in this instance is applicable even to the lower alkanes, if it is postulated that the reacting species are excited $N(^2D)$ atoms[69]. An interesting feature is that it has been proved that in systems of this type organic radicals do not influence the reaction rate[68] and that the addition of nitric oxide had little influence on the yield of HCN[69].

3. REACTIONS OF EXCITED NITROGEN MOLECULES

The electronic excitation of a molecule generally makes it more reactive. This is due to a number of factors[108]: (1) on excitation, unpairing of one of the electron pairs of the molecule takes place, facilitating the attachment of another molecule with an unpaired electron; (2) the excited electron is less firmly held by the molecule, so that the reaction of the excited molecule with an electrophilic reagent is facilitated; and (3) the excited electrons sometimes play little part in chemical bonding, so that the energy required for dissociation of the molecule is decreased. It is known[109], however, that simple excited molecules are very rarely the initial centres of chemical reactions. We should therefore not expect reactions of excited nitrogen molecules with organic molecules to be very widespread. This problem has been insufficiently studied by experiment. Photochemical study of nitrogen is difficult, since N_2 absorbs light only with $\lambda < 1450$ Å (8.546 eV) and its absorption cross-section in the $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$ bands is less than 4×10^{-21} cm^2.[110] Thus information on the reactions of excited nitrogen molecules is very limited and is conjectural in character, since it has been obtained indirectly, chiefly in the study of the reactions of active nitrogen. Direct photo-activation of a mixture of nitrogen and methane at a pressure of 5–8 mmHg was achieved by Dodonova[111]. Light from a hydrogen lamp with $\lambda > 1250$ Å and intensity 10^{15}–10^{16} photon s^{-1} was used for the photo-activation. The formation of HCN was detected under these conditions.

Study of the reactions of active nitrogen with hydrocarbons has revealed facts whose explanation required the assumption that active nitrogen contains excited N_2^* molecules, which react with organic molecules[34,38,52,112]. It has been proved that the N_2^* molecules react with CH_4,[57] C_2H_6,[51,57,59] $C(CH_3)_4$,[59] C_2H_4,[51] and CCl_4.[49] Since the conditions under which the reactions take place with the participation of N_2^* give the same products as the conditions under which the chief reagent is atomic nitrogen, it is assumed that second-order collisions with N_2^* molecules excite organic molecules; these subsequently dissociate to form radicals, which react with atomic nitrogen in the usual way[51,59]. The reaction mechanism can then be represented as follows:

$$N_2^* + RH \rightarrow N_2 + RH^* \quad (15)$$

$$RH^* \rightarrow R + H \quad (16)$$

$$R + N \rightarrow HCN \text{ and other products} . \quad (17)$$

It is apparently possible that in a number of instances the participation of N_2^* in reactions with organic molecules may alter the mode of these reactions. Thus in the reaction of active nitrogen with CH_4, C_2H_6, and C_2H_4 below 150°C a considerable increase in the yield of NH_3 compared with the yield of HCN has been observed[51,57]. This was attributed to the participation of nitrogen in excited-molecule reactions[51]. The excited state of N_2^* reacting with hydrocarbons has not been reliably identified. It is usually assumed, however, that long-lived excited states of the molecules are most important in chemical reactions. Table 4, taken from a paper by Phillips[113], gives the long-lived states of molecular nitrogen. Of these, $A^3\Sigma_u^+$, $^3\Delta_u$, and $a^1\Pi_g$ have been detected in the afterglow of nitrogen, and the $^5\Sigma_g^+$ state has been postulated[64]. No definite proof has been obtained for the presence of the $^3\Delta_u$ state in active nitrogen; it was selected as the upper state of the so-called Y series recently discovered in the afterglow of nitrogen[45,114]. Here a choice was made between the $^3\Delta_u$ and $^3\Sigma_u^-$ states. Later results[115] indicated that the upper state in this series is more likely to be $^3\Sigma_u^-$ than $^3\Delta_u$. If $N_2(^3\Delta_u)$ molecules are present in active nitrogen, their concentration should be very low, since this state is apparently readily deactivated in collisions with nitrogen molecules in the ground state[116]. Thus the part played by $N_2(^3\Delta_u)$ in the reactions of active nitrogen with organic molecules cannot be important.

Nothing definite can be said regarding the part played by the excited $^5\Sigma_g^+$ state, since there are no experimental data. Estimates of the lifetime of N_2^* molecules reacting with organic molecules[35,51] gave values slightly greater than $\tau_{emission}$ for the $a^1\Pi_g$ state, excluding the possibility that this state takes part in the reactions with hydrocarbons. The properties of $N_2(A^3\Sigma_u^+)$ molecules, however (the long lifetime, the difficulties associated with the transfer of energy to nitrogen molecules in the ground

TABLE 4. Long-lived states of molecular nitrogen*.

State	Energy ($v = 0$), kcal mole^{-1}	D^0, kcal mole^{-1}	$\tau^*_{emission}$, s	References
$X^1\Sigma_g^+$	0	225	—	
$A^3\Sigma_u^+$	142	83	2.6×10^{-2}	39
			1	13,36,119–121
			0.2–50	122
			12 ± 2.4	123
$^3\Delta_u$	[172]	[107]	1–2	124,125
$a^1\Pi_g$	196	138	1.7×10^{-4}	38,39
$a'^1\Sigma_u^-$	(202)	(132)	4×10^{-2}	39
$^5\Sigma_g^+$	(222)	(3)		
$[^1\Sigma_g^+]$	[(280)]	[(182)]		

* Predicted states or values are given in square brackets, doubtful values are given in parentheses, and the asterisk at the lifetime values indicates that they were introduced into the table by the author.

state [13], and their ready deactivation in collisions with impurities [81,117], make their participation in the reactions of active nitrogen with organic molecules extremely probable, as suggested by Winkler and coworkers [57]. This is confirmed by the competition between the reactions of hydrocarbons and ammonia with active nitrogen [49,51,57], since we now have a considerable amount of evidence that the $A^3\Sigma_u^+$ state of molecular nitrogen is responsible for the decomposition of ammonia in active nitrogen [35]. Safrany et al. [106,118] cast doubt on the initiating role of $N_2(A^3\Sigma_u^+)$ molecules in the reactions of active nitrogen both with organic molecules and with NH_3. They showed, in particular, that an increase of the concentration of $N_2(A^3\Sigma_u^+)$ in active nitrogen as a result of the recombination of N atoms catalysed by a metal surface does not alter the rate of decomposition of hydrocarbons and NH_3. [106,118] The decomposition of ammonia by paramagnetic non-atomic species present in active nitrogen has been confirmed, however [35]. The authors cited consider that these species are $N_2(A^3\Sigma_u^+)$ molecules. There are thus a number of indications that it is the $N_2(A^3\Sigma_u^+)$ species which reacts with organic molecules.

TABLE 5. Types of reaction of nitrogen ions with organic molecules.

Reaction No.	Reaction	Energy of ions, eV	Type of reaction	Refs.
1	$N_2^+ + CH_4$	1000	Dissociative charge transfer	127,128
2	$N_2^+ + CD_4 \rightarrow N_2D^+ + CD_3$	—	Transfer of heavy species	129
3	$N_2^+ + C_2H_6 \rightarrow N^+ + N + C_2H_6$	5000	Dissociation induced by collision	130
4	$N_2^+ + C_2H_4 \rightarrow N^+ + N + C_2H_4$	5000	ditto	130
5	$N_2^+ +$ aromatic compounds	7—500	Dissociative charge transfer	127
6	$N_2^+ + CH_3COOCH_3$	110—150	ditto	131
7	$N_2^+ + CCl_4$	14—150	Transfer of heavy species and molecular rearrangement	132
		150—200	Dissociative charge transfer	132
8	$N_2^{2+} + CCl_4$	3—200	ditto	132
9	$N^+ + CH_4$	5000	»	133
10	$N^+ + CCl_4$	3—30	Transfer of heavy species and molecular rearrangement	89,132
		30—200	Dissociative charge transfer	89,132
11	$N^+ + CF_4$	3—200	ditto	89
12	$N^+ + CF_3Cl$	3—200	»	89

4. REACTIONS OF NITROGEN IONS

a. Positively charged ions. The ion-molecule reactions of compounds of various classes are now being studied extremely intensively. Data on the ion-molecule reactions of nitrogen with organic molecules are still limited, however. There is published information on the reactions of N_2^+, N_2^{2+}, and N^+ ions with organic compounds of various classes: alkanes (CH_4, C_2H_6), alkenes (C_2H_4), aromatic compounds [C_6H_6, $C_6H_5CH_3$, $C_6H_5CH(CH_3)_2$], ketones (CH_3COCH_3), and halogen-substituted alkanes (CCl_4, CF_4, CF_3Cl). All these studies have been carried out in mass-spectrometer ion sources. All the above reactions, except the reaction with CD_4, [129] were studied by bombarding the organic molecules in the gaseous phase with nitrogen ions obtained in a separate ion source: the reaction with deuteriomethane, however, was carried out in an ionisation chamber, in which a mixture of deuteriomethane and nitrogen was ionised with fast electrons, and the reactions of the ions formed were studied. In other words, the methods used were those of external and internal ionisation, using the nomenclature proposed by Tal'roze [126].

Dissociative charge transfer or ion dissociation processes, induced by collision, are most characteristic of the reactions of positive nitrogen ions with organic molecules in the ranges of ion energies studied (see Table 5). Dissociative charge transfer gives a spectrum of organic fragment ions, and there is a tendency for the ions formed in greatest yield to be those which best satisfy the requirements of the resonance principle, that is the ion whose formation is most intensive is the one for which the absolute magnitude of the heat of formation Q is minimal [$Q \simeq$ (energy of recombination of the primary ion with an electron) – (appearance potential of the fragment ion)] [128]. Superimposed on this tendency, however, is the requirement that the corresponding fundamental reaction be exothermic [128]. Both of these requirements reflect the general laws governing ion – molecule reactions of this type [138].

Transfer of heavy species has been observed only in three instances (reactions 2, 7, and 10 in Table 5), where formation of the ions N_2D^+, NCl^+, $NCCl^+$, and NC^+ was observed; it may also be assumed that in reaction 6 some ions also contain nitrogen. In the last instance, however, not all the ions in the resultant mass spectrum were identified, and insufficient justification was obtained for the suggestion put forward. Evidence in support of the suggestion is provided by the following considerations: some of the fragments do not fit into the scheme proposed by the authors cited to explain the mass spectrum, and the molecular weights of these fragments suggest that they contain nitrogen; for example, the value $m/e = 29$ may correspond to the N_2H^+ ion. A small quantity of N_2H^+ ions was also observed in reactions 5. The intensity of the nitrogen-containing ions in this instance, however, was low compared with the ions resulting from charge transfer. The kinetics of the reactions of nitrogen ions with organic molecules have not been studied. The single exception is the reaction

$$N_2^+ + CD_4 \rightarrow N_2D^+ + CD_3 \qquad (18)$$

for which the cross-section is found to be about 4×10^{-16} cm^2 molecule^{-1} ($k \simeq 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) [88]. The studies which have been carried out are as yet insufficient to enable any conclusions to be reached regarding the part played by ion-molecule reactions in the formation of nitrogen-containing organic products during radiolysis. The available data indicate, however, that the formation of nitrogen-containing fragment ions depends both on the energy of the ions and on the chemical nature of the molecules and ions. It may therefore be expected that there exist systems or conditions, in which ion-molecule exchange reactions between nitrogen and organic molecules take place to a significant extent. The absence of such processes in most of the reactions studied can be attributed, for example, to the fact that the studies were carried out using ions whose kinetic energies were too large, whereas the transfer of heavy species in ion-molecule reactions most probably takes place at low energies [138].

b. Negatively charged nitrogen ions. The negative nitrogen ions N^- and N_2^- have not been detected in the ground state, due to the very low electron affinity of both atomic and molecular nitrogen. The formation of an N^- ion in the excited state by the attachment of an electron to an excited nitrogen atom is possible [134-136]. The excited

$N^-(^1D)$ and $N^-(^1S)$ states are metastable, but their possible breakdown as a result of self-ionisation often hinders even the experimental detection of these ions[95]. Accordingly, ion-molecule reactions with the participation of negative nitrogen ions are unknown.

The azide ion N_3^-, formed by the dissociation of NaN_3, exists in solutions. If undergoes photochemical reactions fairly readily; for example, it reacts with water with the formation of N_2, NH_2OH, N_2H_4, and NH_3 on irradiation by light with $\lambda = 2540$ Å,[137] but as yet nothing is known of its reactions with organic molecules.

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