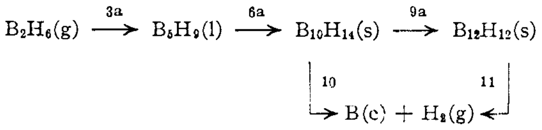
values generally have low vapor pressures, there will be a reduced drive toward loss of H_2 from the condensed phase. This tendency also will be reduced by an appropriate selection of solvents for A. We have, therefore, included in Table II estimated free energy increments for the reactions



$$\begin{tikzcd} B_2H_6(g) \arrow[r, "3a"] & B_5H_9(l) \arrow[r, "6a"] & B_{10}H_{14}(s) \arrow[r, "9a"] \arrow[d, "10"] & B_{12}H_{12}(s) \arrow[dl, "11"] \\ & & B(c) + H_2(g) & \end{tikzcd}$$

ITHACA, N. Y.

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Ionization and Dissociation of Hydrazoic Acid and Methyl Azide by Electron Impact

BY J. L. FRANKLIN,[1] VERNON H. DIBELER, ROBERT M. REESE AND MORRIS KRAUSS

RECEIVED JULY 15, 1957

Relative abundances, appearance potentials and kinetic energy studies are reported for the principal positive and negative ions of hydrazoic acid and methyl azide. Probable ionization dissociation processes are outlined consistent with the observed and computed energetics and with adiabatic correlation rules. Bond dissociation energies and heats of formation of radicals and radical ions are calculated and compared with previously reported values. A 37 kcal./mole activation energy barrier to decomposition at room temperature is indicated for hydrazoic acid by the observed low value for $D(HN-N_2)$. Consideration of the various trinitrogen species results in the conclusions that both N_3^+ and N_3^- ions are stable entities whereas N_3 must be very unstable if it exists at all.

Introduction

Although the literature of electron impact phenomena includes mass spectrometric studies of a variety of organic and inorganic nitrogen compounds, it does not include data on the azides. These interesting compounds are generally unstable and frequently capable of explosive decomposition. The simplest azide, hydrazoic acid, is reported by Rice and co-workers[2,3] to undergo decomposition thermally or by electric discharge to give the imine radical, NH. The significance of the latter as a component in ultra-energy rocket fuels has been investigated by Baum, *et al.*,[4] although these workers find no evidence for the imine radical from HN_3. For these reasons, and as a preliminary step in the mass spectrometric study of the decomposition of hydrazoic acid, it was considered of interest to examine the bond strengths and ion energetics of certain simple azides. Accordingly, the present study was undertaken.

Experimental

Apparatus.—Measurements were made by means of a modified General Electric 60° sector-field mass spectrometer with a 6-inch radius of curvature. The modified Nier-Type ion source included a heavy-walled, relatively gas-tight ionization chamber designed for improved temperature distribution in the ionizing region and a favorable pressure differential between ionizing region and filament region. Temperature of the ion source was not regulated other than by maintaining constant filament temperature.

The filament emission was manually controlled and maintained constant by a regulated d.c. power supply. The electron beam was collimated by a source magnet field of about 150 gauss. The ionizing voltage (electron accelerating voltage) was selected by means of a precision voltage divider providing minimum voltage increments of 0.01 v. in the range of 0 to 100 v.

The analyser tube was operated at high voltage while the ion source was maintained near ground potential. A variable biasing voltage applied to the source permitted observations of stopping potentials for ions formed with excess kinetic energy. Necessary changes in the ion collector assembly essentially followed the suggestions of Fox and Hipple.[5]

The ion detection circuit included an Applied Physics Corporation Vibrating Reed Electrometer, Model 31, and a Leeds and Northrup Speedomax recorder. Minimum reproducible ion currents of 10^{-14} amp. were recorded using a 10^{11} ohm input resistor.

Procedure.—Conventional mass spectrometric techniques and procedures were used in sample introduction. Mass spectra were obtained for 70 v. electrons by continuously varying the ion deflecting magnetic field while maintaining constant ion accelerating voltage. Appearance potentials of the positive ions were evaluated from semi-log plots of ion current *versus* ionizing voltage for the unknown ion and the calibrating gas, argon. Curves were normalized and uncertainties estimated as previously described.[6] Appearance potentials of negative ions were evaluated from linear plots of ion current *versus* ionizing voltage. The latter scale was calibrated by measuring the maximum of the resonance attachment peak for the unknown ion compared with the maximum of the resonance attachment peak for the Cl^- ion of HCl.[7]

Materials.—Hydrazoic acid was prepared by the reaction of 60–80% sulfuric acid with solid or aqueous sodium azide using vacuum techniques. The product vapors were collected in a sample bulb fitted with a stopcock and demountable standard taper for attachment to the mass spectrometer. Mass spectrometric analysis indicated a high purity material (~99%). However, the use of concentrated sulfuric acid on dry sodium azide almost invariably resulted in a product grossly contaminated with impurities not easily separable by simple bulb-to-bulb distillation.

Methyl azide was prepared by the reaction of dimethyl sulfate and aqueous sodium azide using vacuum techniques. Mass spectrometric analysis of the product vapors indicated dimethyl ether as a major impurity. To avoid the possible danger of handling the relatively large amounts required for fractional distillation, the purification was accomplished by passing the crude material through a gas chromatograph. The effluent vapors desorbed from the column easily were diverted to collection bulbs when the detector indicated evolution of the methyl azide fraction. Mass spectrometric analysis gave no indication of impurities in the separated fraction other than a trace of water vapor.

Results

Tables I and II give the relative abundances of ions from hydrazoic acid and methyl azide, respectively, together with the appearance potentials of

---

[1] Guest Scientist on leave from the Humble Oil and Refining Co., Baytown, Texas.

[2] F. O. Rice and M. Freamo, THIS JOURNAL, **73**, 5529 (1951).

[3] F. O. Rice and C. Grelecki, *ibid.*, **79**, 1880 (1957).

[4] L. Baum, H. Graff, E. I. Hormats and G. Moe, Air Force Office of Scientific Research, Report No. 1149, July, 1956.

[5] R. E. Fox and J. A. Hipple, *Rev. Sci. Instr.*, **19**, 462 (1948).

[6] V. H. Dibeler and R. M. Reese, *J. Research Natl. Bur. Standards*, **54**, 127 (1955).

[7] R. E. Fox, *J. Chem. Phys.*, **26**, 1281 (1957).

TABLE I

RELATIVE ABUNDANCES AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF HYDRAZOIC ACID

Process	Relative abundance, (%)	A.P. (e.v.)	ΔH_f (ion), kcal./mole	Remarks
$HN_3 \rightarrow HN_3^+$	100.0	10.3 ± 0.2	308	
$\rightarrow N_3^+ + H$	5.8	16.0 ± .2	388	I_p (N_3) $\approx$11.6 v.
$\rightarrow N_2H^+ + N$	8.3	13.8 ± .2	278	
$\rightarrow N_2^+ + NH$	7.3	16.0 ± .1	81[a]	$D(HN\text{–}N_2)$ = 9 kcal./mole
$\rightarrow N_3^{++} + H$	2.6	....	..	....
$\rightarrow NH^+ + N_2$	16.8	14.4 ± .2	404	I_p (NH) $\leqq$ 14 v.
$\rightarrow N^+ + N_2 + H(?)$	4.9	19.7 ± .3	474	Excess energy
$\rightarrow N_3^- + H$	2.5	1.1 ± .2	45	Resonance capture process EA(N_3) = 72 kcal./mole
$\rightarrow NH^- + N_2(?)$	2.5	0.8 ± .3	90	Resonance capture process probably involves excess energy

[a] ΔH_f neutral products of reaction.

TABLE II

RELATIVE ABUNDANCES AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS OF METHYL AZIDE

Process	Relative abundance, (%)	A.P. (e.v.)	ΔHf (ion), kcal./mole	Remarks
$CH_3N_3 \rightarrow CH_3N_3^+$	48.3	9.5 ± 0.1	276	....
$\rightarrow CH_2N_3^+ + H$	0.3	....	..	....
$\rightarrow HCN_3^{++} + 2H(?)$	3.2	~34	..	....
$\rightarrow N_3^+ + CH_3$	1.9	17.6 ± .5	431	Contains excess energy
$\rightarrow HCN_2^+ \ldots$	0.2	....	..	....
$\rightarrow CH_3N^+ + N_2(?)$	3.4	....	..	....
$\rightarrow CH_2N^+ + H + N_2$	100.0	10.5 ± .1	247	....
$\rightarrow HCN^+ + H_2 + N_2$	32.0	13.6 ± .5	371	....
$\rightarrow CN^+ + \ldots$	2.7	....	..	....
$\rightarrow NH_2^+ \ldots$	4.0	....	..	....
$\rightarrow CH_3^+ + N_2 + N(?)$	28.4	14.1 ± .1	120[a]	$D(CH_3\text{–}N_3)$ = 95 kcal./mole (?)
$\rightarrow N^+$ or $CH_2^+(?)$	15.4	....	..	....
$\rightarrow CH^+ + \ldots$	7.4	....	..	....
$\rightarrow C^+ + \ldots.$	3.5	....	..	....
$\rightarrow N_3^- + CH_3$	0.4	1.1 ± .3	50	Resonance capture process EA = 72 kcal./mole

[a] ΔH_f neutral products of reaction.

the more abundant ions. Abundances are given relative to the most abundant ion and for positive ions were measured using 70 v. electrons. The abundances of the negative ions are relative to the most abundant positive ion at 70 v. but are measured at the electron energy giving maximum ion current for the negative ion. The tables also give our conclusions as to the probable processes from which the various ions are formed and the heats of formation of the ions or radicals as calculated from the appearance potentials and known thermochemical data. In some cases the conclusions are also based upon adiabatic correlation rules. The importance of correlation rules in analyzing reactions occurring in a mass spectrometer has been discussed by McDowell[8] and Laidler.[9] Schuler[10] has shown how they can be applied to simple polyatomic and diatomic complexes. In the application of correlation rules the transitions that are not allowed were seen to be forbidden by the spin conservation rules. Orbital correlation rules were not employed as consideration of vibational excitation and/or the probable low symmetry of the activated complex at some point in dissociation would render any orbital restrictions invalid. The states ascribed to the molecules in some cases seem to us the probable ones under those reaction conditions and of course are related only to the electronic state of the molecule or atom.

In calculating heats of formation, $\Delta H_f(HN_3)$ was taken as 71.7 kcal./mole as determined by Gray and Waddington.[11] No values of $\Delta H_f(CH_3N_3)$ could be found in the literature. However, heats of combustion of the cyclohexyl and cyclopentyl azides have been determined by Fagley and Myers.[12] From these values a ΔH_f = 57 kcal./mole for methyl azide was estimated using the group equivalent method of Franklin.[13]

Molecule Ions.—Spectroscopic ionization potentials for hydrazoic acid and methyl azide have not been published. The electron impact values reported here are the "vertical" ionization potentials as required by the Franck-Condon principle and are considered upper bounds to the spectroscopic or "adiabatic" ionization potentials. The ionization potential of HN_3 (10.3 ± 0.2 e.v.) is slightly

---

(8) (a) C. A. McDowell, *Trans. Faraday Soc.*, **50**, 423 (1954); (b) "Applied Mass Spectrometry," The Institute of Petroleum, London, 1954, pp. 129-153.

(9) K. J. Laidler, *J. Chem. Phys.*, **22**, 1740 (1954).

(10) K. E. Schuler, *ibid.*, **21**, 624 (1953).

(11) P. Gray and T. C. Waddington, *Proc. Roy. Soc. (London)*, **A235**, 106 (1956).

(12) T. F. Fagley and H. W. Myers, THIS JOURNAL, **76**, 6001 (1954).

(13) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

greater than that of methyl azide (9.5 ± 0.1 e.v.) which may be ascribed to the greater ionic character of the latter with a consequent decrease in binding of electrons localized mainly on the N_3 group. The electron evidently is removed from an antibonding orbital as all of the bonds of HN_3^+ appear to be stronger than those in HN_3.

N_3^+.—The appearance potential of N_3^+ from HN_3 leads to a value of 388 kcal./mole for the heat of formation of the ion. The value from methyl azide is 43 kcal./mole higher. We are inclined to think that the lower value is more nearly correct. The abundance of the N_3^+ ion from HN_3 is considerably greater than that from methyl azide and hence the appearance potential should be more accurate. Further, one would expect from Stevenson's rule[14] that the process forming N_3^+ would not involve excess kinetic energy in the case of the HN_3 and probably would in the case of the methyl azide. Unfortunately this rule is not without exceptions. The adiabatic correlation rules allow both HN_3^+ and the decomposition products to be in their ground states so the probable process is

$$HN_3^+(^2A'') \longrightarrow N_3^+(^3\Sigma_g^-) + H(^2S_g)$$

where it is assumed that N_3^+ is linear.

N_2H^+.—The appearance potential and heat of formation of this ion from hydrazoic acid are surprisingly low, although we know of no published measurements with which to compare this value. A low appearance potential resulting from an N^- ion formed by an ion-pair process is ruled out. Schissler and Stevenson have reported the reaction $N_2^+ + H_2 = N_2H^+ + H$[15] as proceeding without activation energy, indicating that the heat of reaction must be zero or exothermic. Assuming it to be zero, $\Delta H_f(N_2H^+)$ is calculated to be 307 kcal./mole which is concordant with our measured value. The reaction may thus be written, for all substances in their ground states

$$HN_3^+(^2A?) \longrightarrow N_2H^+(^3?) + N(^4S_u)$$

It is emphasized that N_2H^+ must be in a triplet state. Walsh's orbital energy diagrams[16] indicate that this ion, which is isoelectronic with HCN, should be $^1\Sigma^+$ in the ground state and, if true, this indicates that the product obtained in our study was electronically excited. Measurements of the appearance potentials of N_2H^+ from other sources are needed to clarify this. The possibility of an excited nitrogen also must be considered.

Ions of m/e = 28.—The ion of mass 28 from HN_3 can only be N_2^+ and since the products are in their ground states, its appearance potential combined with the known ionization potential of N_2 leads to a value of 81 kcal./mole for $\Delta H_f(NH)$ and of 9.2 kcal./mole for $D(N_2\text{–}NH)$ and of 83 kcal./mole for $D(N\text{–}H)$. Pannetier and Gaydon[17] obtained 88 kcal. for the latter value from a spectroscopic study of the explosive decomposition of HN_3. One might expect the mass 28 ion from methyl azide also to be N_2^+. However, the appearance potential of 10.5 e.v. is far too low, and in the absence of an ion-pair process we must conclude that it is CH_2N^+. Obviously, it is impossible to know what neutral fragments are formed in this reaction. However, $N_2 + H$ appeared to us to be the most reasonable under the circumstances and lead to the maximum value for $\Delta H_f(CH_2N^+)$. It is of interest that Collin's values[18] of the appearance potential of ions of mass 28 from several amines can best be interpreted as corresponding to the CH_2N^+ ion and $\Delta H_f(CH_2N^+)$ calculated from Collin's data by Field and Franklin[19] is about 250 kcal./mole in good agreement with the value obtained in this study.

HCN^+.—The mass 27 ion from methyl azide can only be HCN^+. If the neutral products are H_2 and N_2, a maximum value of the heat of formation is obtained. This is approximately 27 kcal./mole greater than that calculated from the ionization potential of HCN. Several observations of the ionization efficiency curve for this ion showed discontinuities near the onset that could correspond to other dissociation processes. These "breaks" contributed to the uncertainty in determining the minimum energy value. On the other hand, it would not be surprising if excess kinetic energy were involved in the minimum dissociation process, and any other combination of neutral fragments would lead to $\Delta H_f(HCN^+)$ considerably lower than the accepted value. Therefore we must conclude that the indicated process with the excess kinetic energy is the more probable one.

NH^+.—We calculate $\Delta H_f(NH^+)$ to be 404 kcal./mole. This is about 33 kcal./mole lower than the value derived from the appearance potential of NH^+ from NH_3 assuming H_2 to be formed concurrently.[20] The ground state of NH^+ is not known but it is either a $^2\pi$ or a $^4\Sigma^-$ state.[21] Furthermore, $HN_3^+(^2A'')$ cannot dissociate into $NH^+(^4\Sigma^-) + N_2(^1\Sigma_g^+)$ but can give $NH^+(^2\pi) + N_2(^1\Sigma_g^+)$. From this it might appear that the ground state of NH^+ is the $^2\pi$ state with the NH^+ from NH_3 involving an excited state and/or some kinetic energy.

If the value for $\Delta H_f(NH^+)$ obtained assuming NH^+ is formed in its ground state from HN_3^+ is used, we obtain an upper limit for $I(NH)$ of 14.0 e.v. However, the fact that the $^4\Sigma^-$ state of NH^+ correlates with the ground state dissociation products lends weight to the assumption that this is the ground state which suggests a different possible reaction path for these processes. McDowell[8b] has pointed out that NH^+ may be obtained from NH_3^+ by the process

$$NH_3^+(^2E') \longrightarrow NH^+(^2\pi) + 2H(^2S_g)$$

---

[14] D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[15] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956). The reaction by which N_2H^+ is formed might well involve $H_2^+ + N_2$, and it is doubtful if one could be certain which reaction actually occurs. The only means of identifying the reaction is to compare the appearance potential of the secondary ion with that of various primary ions. Unfortunately the ionization potentials of H_2 and N_2 are almost identical. However, this would not change the conclusions concerning $\Delta H_f(N_2H^+)$.

[16] A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

[17] G. Pannetier and A. G. Gaydon, *J. chim. phys.*, **48**, 221 (1951).

[18] J. Collin, *Bull. soc. chim. Belges*, **62**, 411 (1953).

[19] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

[20] M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **58**, 340 (1940).

[21] M. W. Feast, *Appl. J.*, **114**, 344 (1951).

However, if the excited NH_3^+ ion first dissociated into an excited triplet NH_2^+ ion then the $^4\Sigma^-$ state of NH^+ could be obtained and probably would be formed with excess kinetic energy sufficiently larger than the excitation energy $^2\pi \rightarrow {}^4\Sigma^-$ of the NH^+ ion to give the lower $\Delta H_f(NH^+)$ in the HN_3 case although for this interpretation we assume the NH^+ ion to be excited. Additional evidence is required for a more confident choice of mechanism.

CH_3^+.—The ion of $m/e = 15$ from methyl azide might be either CH_3^+ or NH^+. The appearance of an $m/e = 16$ isotope peak, however, indicates it to be CH_3^+. The appearance potential of CH_3^+ when combined with the value of 262 kcal./mole for $\Delta H_f(CH_3^+)$ leads to a heat of formation for the neutral products of reaction of 120 kcal./mole. This value is greater than $\Delta H_f(N_2) + \Delta H_f(N)$ and so we are inclined to think N_2 and N rather than the N_3 radical, are formed. However, it must be recognized that there may be an activation energy hindering the decomposition of N_3 which would be sufficiently great to prevent this decomposition under conditions existing in the mass spectrometer. It is obvious, however, that only such an activation energy can stabilize the N_3 radical if it exists. The N_3 radical is probably formed in a doublet ground state and if linear is in a $^2\pi_g$ state which cannot dissociate unimolecularly into ground state products; *i.e.*

$$N_3(^2\pi_g) \xrightarrow{\;\;H\!\!\!\!-\;\;} N_2(^1\Sigma_g^-) + N(^4S_u)$$

It can, of course, dissociate into excited states of these products. It is of interest that the value obtained in this study is in quite good agreement with 116 kcal./mole obtained for $\Delta H_f(N_3)$ by Gray and Waddington[22] from lattice energies.

N^+.—The only reasonable mechanism for the formation of N^+ from HN_3 involves the concomitant formation of H and N_2. Correlation rules allow all products to be in their ground states. The heat of formation of N^+ calculated assuming this mechanism is about 26 kcal./mole above the accepted value, and so we must conclude that the products probably are formed with some excess kinetic energy.

HCN_3^{++}.—The stable ion of $m/e = 27.5$ observed in the methyl azide spectrum can only be a doubly charged ion of mass 55 and must be HCN_3^{++}. It is unexpected that there is no evidence for an HCN_3^+ ion at any electron energy in the range covered. The reaction indicated for the formation of HCN_3^{++} is arbitrary.

N_3^-.—N_3^- ions were formed at quite low voltages from both HN_3 and CH_3N_3. The process in each case involves resonance capture. We were unable to find evidence for the formation of N_3^- by a pair production process. The appearance potential of N_3^- was taken as the maximum of the ion abundance curve and the absolute value of the appearance potential was obtained by comparing it with the maximum Cl^- ion from HCl. The values obtained in this way lead to values of $\Delta H_f(N_3^-)$ of 45 and 50 kcal./mole, respectively, from HN_3 and CH_3N_3.

The average value of $\Delta H_f(N_3^-)$ agrees fairly well with that of Gray and Waddington.[22] Taking the value for the $\Delta H_f(N_3)$, obtained in this research, the value 72 kcal./mole is derived for the electron affinity of N_3, again in fair agreement with the value of 81 kcal. reported by Gray and Waddington.[22] Since adiabatic correlation rules allow reactant and products to be in their ground states the process involved is very probably

$$HN_3^-(^2A') \longrightarrow N_3^-(^1\Sigma_g^+) + H(^2S_g)$$

where the electronic state of the parent ion is determined by the states of the products.

NH^-.—This ion is formed from HN_3 by resonance capture and no evidence could be found for a pair production process. We were unable to find an analogous CH_3N^- ion from CH_3N_3.

The appearance potential of NH^- from HN_3 was found to be 0.8 v. If this is combined with our value of 0.4 e.v. for $D(HN-N_2)$, we obtain an apparently negative value for the electron affinity of NH. However, this ion is relatively abundant, compared with usual negative ion abundances. Thus it is probable that it has a positive electron affinity and that the electron is firmly bound to the radical. The possibility that $EA(NH) < 0$ but that the ion is stable cannot be ruled out as the ion may be formed in a vibrational level such that a Franck-Condon transition between NH and NH^- is improbable.

The correlation rules allow the reaction $HN_3^-(^2?) \rightarrow NH^-(^2\pi) + N_2(^1\Sigma_g^+)$ but there is little information concerning the energy levels of NH^-, which renders interpretation difficult. The $NH^-(^2\pi)$ state cannot correlate with the ground state of the dissociation products $N(^4S_u) + H^-(^1S_g)$ but can with $N(^2D_u) + H^-(^1S_g)$ which is 2.4 e.v. above the unallowed level. No level involving N^- has been considered as there is no evidence for the existence of this ion. However, such a state is probably lower than the $N(^2D_u)$ level.[23] Dissociation of the molecule to such a state would then involve detachment of an electron and production of neutral atom species. For NH to have a positive electron affinity would require $D(NH^-) > D(NH) + 1.7$ e.v. where 1.7 is the excitation energy of $N(^2D_u)$ minus EA(H). This is unlikely as the added electron is in a non-bonding or slightly antibonding orbital. It is possible, of course, that NH^- is formed in the ground electronic state but with excess kinetic energy. We are forced to conclude that this is the more probable process.

Discussion

It is interesting to consider the very small value of $D(HN-N_2)$. If this were all of the activation energy for the bond-breaking reaction, the molecule HN_3 could not exist at ordinary temperatures. In fact, this material can be stored as a gas at room temperature and reduced pressures for several days without serious decomposition, and other workers report no difficulties in storing the material. Obviously there is an additional energy barrier to decomposition. Consideration of the adiabatic cor-

---

(22) P. Gray and T. C. Waddington, *Proc. Roy. Soc.* (*London*), **A235**, 481 (1956).

(23) L. M. Branscomb and S. J. Smith, *J. Chem. Phys.*, **25**, 598 (1956).

relation rules shows that the reaction

$$HN_3(^1A') \longrightarrow NH(^3\Sigma^-) + N_2(^1\Sigma_g^+)$$

giving products in the ground state is not allowed. However, reaction can proceed to the lowest singlet state of NH, thus

$$HN_3(^1A') \longrightarrow NH(^1\Delta) + N_2\,(^1\Sigma_g^+)$$

The $^1\Delta$ state is about 28 kcal./mole above the $^3\Sigma^-$ state of NH and thus would increase the activation energy for this decomposition to about 37 kcal./mole. A similar situation is discussed for the N_3 radical in a previous section. This activation barrier would render hydrazoic acid fairly stable at room temperature but would permit rapid decomposition above about 200°. We plan to study the kinetics of this reaction in an effort to determine this activation energy more definitely.

Consideration of the various tri-nitrogen entities shows that both N_3^- and N_3^+ are quite firmly bonded, but that N_3, if it exists at all, must be very unstable. Thus, $D(N_2\text{-}N^-)$ must be approximately equal to the electron affinity of N_3 and $D(N_2\text{-}N^+)$ is approximately 83 or 59 kcal./mole depending on whether N or N_2 retains the charge. On the other hand, apparently $D(N_2\text{-}N) \leqslant 0$. Presumably this is another example of the greater stability of systems having even numbers of electrons. It is striking that either adding or removing an electron permits formation of a firm bond where none otherwise exists.

Acknowledgment.—The authors are indebted to Charles R. Yokley of the Engine Fuels Section for the purification of the methyl azide by gas chromatography and to Fred L. Mohler for helpful suggestions and discussion throughout the course of the work.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Diffusion in Sugar Solutions. IV. The Onsager Diffusion Coefficients for Glucose Diffusing in Sucrose Solutions

BY F. E. WEIR AND MALCOLM DOLE

RECEIVED OCTOBER 1, 1956

Height–area diffusion coefficients and reduced second moments have been measured at 25 and 35° for aqueous solutions containing on the average 60.5% sucrose, 0.5% glucose and 39% water. From these values the main and cross term diffusion coefficients as defined by Baldwin, Dunlop and Gosting have been calculated using the recently published method of Fujita and Gosting. Equations relating these diffusion coefficients to those defined by Onsager are given and the Onsager diffusion coefficients calculated.

I. Introduction

This paper represents the fourth in a series on diffusion in concentrated sucrose and glucose solutions and their mixtures. Having previously studied sucrose[1] and glucose[2] in binary systems with water as solvent and the diffusion of sucrose in the presence of glucose,[3] in this work the diffusion of glucose was studied in the presence of sucrose.

During the course of this work an important paper by Fujita and Gosting[4] appeared in which a mathematical technique was developed by which all four diffusion coefficients defined by the relations (first introduced by Baldwin, Dunlop and Gosting[5]), could be calculated. In eq. 1 the sub-

$$\frac{\partial c_1}{\partial t} = \mathfrak{D}_{11}\frac{\partial^2 c_1}{\partial x^2} + \mathfrak{D}_{12}\frac{\partial^2 c_2}{\partial x^2} \qquad \text{(1a)}$$

$$\frac{\partial c_2}{\partial t} = \mathfrak{D}_{22}\frac{\partial^2 c_2}{\partial x^2} + \mathfrak{D}_{21}\frac{\partial^2 c_1}{\partial x^2} \qquad \text{(1b)}$$

script 1 refers to sucrose and the subscript 2 to glucose. $\mathfrak{D}$ is the diffusion coefficient in cm.²/sec., x the distance from the initial boundary, c the solute concentration in moles/cc. and t the time.[6]

In this paper measured diffusion coefficients will be indicated by script $\mathfrak{D}$'s while coefficients calculated from the Onsager relations (see below) will be designated by Roman D's.

Experiments were conducted that made possible the use of Fujita–Gosting method. Experiments similar to those of Clarke and Dole[3] were also attempted, but with uncertain success. Included in the present paper are recalculated values of Clarke and Dole who inadvertently failed to add unity to the extrapolated j values to obtain j_m. (for definition see reference 1). The numerical values of Clarke and Dole were changed slightly by this correction.

II. Reciprocal Relations of Onsager

Some years ago, Onsager[7] generalized Fick's law of diffusion to systems of more than two components. For unidirectional diffusion in a system of 3 components

$$J_0 = -\,\mathrm{D}_{00}\frac{\partial c_0}{\partial x} - \mathrm{D}_{01}\frac{\partial c_1}{\partial x} - \mathrm{D}_{02}\frac{\partial c_2}{\partial x} \qquad \text{(2a)}$$

$$J_1 = -\,\mathrm{D}_{10}\frac{\partial c_0}{\partial x} - \mathrm{D}_{11}\frac{\partial c_1}{\partial x} - \mathrm{D}_{12}\frac{\partial c_2}{\partial x} \qquad \text{(2b)}$$

$$J_2 = -\,\mathrm{D}_{20}\frac{\partial c_0}{\partial x} - \mathrm{D}_{21}\frac{\partial c_1}{\partial x} - \mathrm{D}_{22}\frac{\partial c_2}{\partial x} \qquad \text{(2c)}$$

---

[1] A. C. English and M. Dole, THIS JOURNAL, **72**, 3261 (1950).

[2] J. K. Gladden and M. Dole, *ibid.*, **75**, 3900 (1953).

[3] D. M. Clarke and M. Dole, *ibid.*, **76**, 3745 (1954).

[4] H. Fujita and L. J. Gosting, *ibid.*, **78**, 1099 (1956).

[5] R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5235 (1955). See also P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5238 (1955).

[6] It should be noted that the cross term coefficients $\mathfrak{D}_{12}$ and $\mathfrak{D}_{21}$ are different if the concentrations are expressed as grams/liter instead of moles/liter as first recognized by P. J. Dunlop. (Private communication from L. J. Gosting.) In this paper the concentrations will always be expressed in moles/liter or moles/cc.

[7] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945). L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932). G. J. Hooyman. *Physica*, **22**, 751 (1956), has also discussed the Onsager reciprocal relations as applied to diffusion and has given this relation for ternary mixtures in terms of four diffusion coefficients.