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Reactions of Gaseous Ions. II. Acetylene

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The gas phase reactions of several organic positive ions with acetylene have been identified and their rates measured. The rates are in approximate agreement with values calculated theoretically. Appearance potentials of several primary ions have been measured to provide energy data necessary for interpretation of certain secondary reactions.

In a recent paper[1] we reported on studies of the reactions of ions from methane and ethylene in a mass spectrometer ion source. The present paper reports the results of studies of the reactions of ions from acetylene. Hinkle, Roberts and Hamner[2] have reported secondary ions from several acetylenes but did not identify the reactions or measure the reaction rates. In this paper we describe experiments by which the reactions leading to the formation of several secondary ions from acetylene were determined and their rates measured.

Results and Discussions

A typical mass spectrum of acetylene at a reservoir pressure of 10.3 mm. is given in Table I. The important secondary peaks are those having *m/e* ratios of 51, 50, 49, 37 and 38. All of these peaks exhibited an approximately second-order pressure dependence and so could not be attributed to impurities. Further, their variation in intensity with repeller voltage clearly showed them to be secondary ions.

TABLE I

MASS SPECTRUM OF ACETYLENE AT 10.3 MM. RESERVOIR PRESSURE ($N = 11 \times 10^{13}$ MOLECULES/CC.) ($V_R = 1$ v.)

m/e	Intensity, arbitrary units	*m/e*	Intensity, arbitrary units
12	510	37	44
13	1590	38	21
14	70	39	4
24	1530	49	55
25	5800	50	750
26	38000	51	930
27	750	52	≈12

In order to identify the reactions by which these secondary products were formed, their appearance potentials were measured in the Westinghouse Type LV mass spectrometer using the techniques described in the previous paper. Firm data have not previously been obtained for the appearance potentials and heats of formation of certain of these ions. In order to interpret the results of our secondary reactions, it was necessary to determine the heats of formation of these ions by measuring their appearance potentials as primary decomposition products. Accordingly, we determined the appearance potentials of the C_3H^+ and C_4H^+ ions from 1,3-butadiene, 1-butyne and vinylacetylene and of the $C_4H_2^+$ and $C_4H_3^+$ ions from vinylacetylene. In addition, for purposes of calibration we measured the appearance potential of the CH^+, C_2^+ and C_2H^+ ions from acetylene. The appearance potentials of these primary ions and the corresponding heats of formation are given in Table II.

Our value for C_2H^+ is in sufficiently good agreement with the value of 17.8 v. reported by Coats and Anderson[3] and Kusch, Hustrulid and Tate.[4] Also, our appearance potential for CH^+ agrees within the accuracy of the measurements with the value of 22.3 v. reported by the latter workers.

We found three values for the appearance potential of the C_2^+ ion from acetylene. The low value of about 13 v., which is quite approximate, is probably attributable to a small amount of pyrolysis on the filament. There were also two quite definite

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[1] F. H. Field, J. L. Franklin and F. W. Lampe, THIS JOURNAL, **79**, 2419 (1957).

[2] Hinkle, Roberts and Hamner, paper presented at meeting of ASTM Committee E-14, Cincinnati, Ohio, May 28–June 1, 1956.

[3] F. H. Coats and R. C. Anderson, THIS JOURNAL, **77**, 895 (1955).

[4] P. Kusch, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **52**, 843 (1937).

TABLE II

APPEARANCE POTENTIALS OF PRIMARY IONS

m/e	Ions from acetylene	*A*p, v.	ΔH_f (ion),[a] kcal./mole
13	$C_2H_2 \rightarrow CH^+ + CH$	21.68	
24	$C_2 \rightarrow C_2^+$	≈13	
	$C_2H_2 \rightarrow C_2^+ + H_2$	18.2	474
	$C_2H_2 \rightarrow C_2^+ + 2H$	22.7	472
25	$C_2H_2 \rightarrow C_2H^+ + H$	17.3	401
	Ions from 1,3-butadiene		
37	$C_4H_6 \rightarrow C_3H^+ + CH_3 + H_2$	12.44	282
	$\rightarrow C_3H^+ + CH_3 + 2H$	18.96	328
49	$C_4H_6 \rightarrow C_4H^+ + 2H_2 + H$	15.75	336
	$\rightarrow C_4H^+ + 5H$	25.30	349
	Ions from 1-butyne		
37	$C_4H_6 \rightarrow C_3H^+ + CH_3 + H_2$	12.59	299
	$\rightarrow C_3H^+ + CH_3 + 2H$	17.62	312
49	$C_4H_6 \rightarrow C_4H^+ + 2H_2 + H$	13.20	292
	$\rightarrow C_4H^+ + 5H$	22.68	303
	Ions from vinylacetylene		
37	$C_4H_4 \rightarrow C_3H^+ + ?$	18.71	?
49	$C_4H_4 \rightarrow C_4H^+ + H_2 + H$	12.13	293
	$\rightarrow C_4H^+ + 3H$	17.02	301
50	$C_4H_4 \rightarrow C_4H_2^+ + H_2$	12.84	361
51	$C_4H_4 \rightarrow C_4H_3^+ + H$	12.59	303

[a] Calculated using heats of formation taken from the API tables.[5] The heat of formation of vinylacetylene was estimated by the method of group equivalents[6] assuming a resonance energy of 4 kcal/mole.

discontinuities in the ion intensity curves, one at 18.2 v. and the other at 22.7 v. The higher value corresponds within experimental accuracy to the 23.3 and 23.9 v. values of Coats and Anderson and Kusch, Hustrulid and Tate. This we attribute to the reaction

$$C_2H_2 \longrightarrow C_2^+ + 2H$$

The lower appearance potential 18.2 v. differs from the higher by almost exactly $D(H_2)$ and accordingly it is reasonable to attribute it to the reaction

$$C_2H_2 \longrightarrow C_2^+ + H_2$$

We are concerned that other investigators have not observed this appearance potential, but in our instrument it was definite and we think the interpretation is a reasonable one.

It was surprising to find the lower appearance potentials for the C_3H^+ ion from 1,3-butadiene and 1-butyne so small. The values appear real, however, and we have no choice but to accept them. In each case we have interpreted the appearance potential as corresponding to the reaction giving the highest heat of formation for C_3H^+. Although there is a discrepancy of 17 kcal./mole between the results from the two sources, the heat of formation nevertheless appears to be in the neighborhood of 290 kcal./mole. Further, the higher appearance potentials, if interpreted as corresponding to the formation of hydrogen atoms instead of H_2, give approximate agreement with this heat of formation of C_3H^+. The literature gives very few measurements of the appearance potential of C_3H^+. The only one capable of unequivocal interpretation is that of Field[7] from cyclopropane. His value of 15.0 v. leads to a heat of formation of C_3H^+ of 307 kcal./mole if one assumes the reaction

$$\text{Cyclo-}C_3H_6 \longrightarrow C_3H^+ + 2H_2 + H$$

More extensive atomization of hydrogen would give unreasonably low heats of formation of C_3H^+. Coats and Anderson[3] obtained a value of 18.4 v. from propyne which would lead to a heat of formation of 416 or 312 kcal./mole depending upon whether the decomposition reaction involved the formation of $H_2 + H$ or 3H. Hissel[8] measured the appearance potential of C_3H^+ from pyrrole, furan and thiophene. The results can be interpreted as corresponding to a heat of formation of C_3H^+ in the neighborhood of 300 kcal./mole, but since the reactions are complicated, any interpretation would be equivocal. It appears then, from all of the available measurements, that a value for the heat of formation of C_3H^+ in the neighborhood of 300 kcal./mole is correct although it is indeed lower than would have been anticipated.

The appearance potentials of the C_4H^+ ion similarly lead to surprisingly low values for the ion's heat of formation. Although again close agreement is not obtained amongst the heats of formation from various sources, we must conclude that the heat of formation of C_4H^+ is in the neighborhood of 300 kcal./mole. Unfortunately, we know of no reliable measurement for the appearance potential from other sources.

In an earlier paper, Franklin and Field[9] reported the appearance potential of $C_4H_2^+$ from vinylacetylene as 12.88 v. Partly for purposes of calibration we remeasured this appearance potential and found excellent agreement with the previous value. This leads to a heat of formation of 361 kcal./mole which is in fair agreement with that which one calculates from ionization potentials reported by Price and Walsh.[10]

Our value for the heat of formation of the $C_4H_3^+$ ion is appreciably lower than that obtained from Coats and Anderson's[3] value as determined from butyne-2. We are inclined to prefer our value since it corresponds to a simpler decomposition.

In Table III, we compare the appearance potentials of ions formed in acetylene by secondary processes with that of the primary ion formed from acetylene by a primary process. From this, it is evident that $C_4H_3^+$ and $C_4H_2^+$ are formed by reaction of $C_2H_2^+$ with acetylene. Further, these two peaks are by far the most intense in the secondary spectrum and undoubtedly correspond to reaction of a very abundant primary ion.

It is of interest that two appearance potentials for the C_4H^+ ion were found. These correspond approximately to the two appearance potentials of C_2^+ from acetylene at 18.2 and 22.7 v. We did not observe a C_4H^+ appearance potential at around 13 v., but this is not surprising since the amount of

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(5) Rossini, Pitzer, Arnett, Braun and Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Institute of Technology Press, Pittsburgh, Pennsylvania, 1953.

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

(7) F. H. Field, *J. Chem. Phys.*, **20**, 1734 (1952).

(8) J. Hissel, *Bull. Soc. Roy. Sci. Liège*, **21**, 457 (1952).

(9) J. L. Franklin and F. H. Field, THIS JOURNAL, **76**, 1994 (1954).

(10) W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

TABLE III

IDENTIFICATION OF SECONDARY REACTIONS

m/e	*A*p secondary ion, v.	*A*p of nearest primary ion from C_2H_2, v.	Probable reaction	ΔH_r,[a] kcal./mole
51	11.07	11.4	$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$	− 16
50	11.38	11.4	$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$	− 10
49	19.2	18.2	$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	−181
49	22.5	22.7	$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	
38	21.3	21.68	$CH^+ + C_2H_2 \rightarrow C_3H_2^+ + H$	−2 to −30
37	22.9	21.68	$CH^+ + C_2H_2 \rightarrow C_3H^+ + H_2$	−109
			or $CH^+ + C_2H_2 \rightarrow C_3H^+ + 2H$	− 5

[a] Calculated using heats of formation of ions taken from the compilation of Field and Franklin[11] and heats of formation of neutral molecules taken from the API tables.[3]

pyrolysis was so small that even the primary C_2^+ peak corresponding to it was very difficult to measure.

The appearance potentials of both the 37 and 38 peaks in the secondary spectrum agree most closely with that of CH^+ and we conclude, therefore, that both of these ions are formed by the reaction of CH^+ with acetylene. Both processes would be exothermic. Further, these secondary peaks are comparatively small and would be expected to arise from a comparatively weak precursor.

In the previous paper,[1] we showed that where two secondary ions arise from a common primary, the reaction can be best interpreted as involving the decomposition of a common activated complex. This is also true of the ions from acetylene. Thus, comparison in Table IV of the relative intensities of $C_4H_3^+$ and $C_4H_2^+$ ions formed as primary decomposition products of C_4H_4 and as secondary products from the reaction of $C_2H_2^+$ and C_2H_2, shows very close agreement. The C_4H^+ is also formed as a primary product from C_4H_4, but appearance potentials indicate that it is not formed in appreciable amounts from the reaction of $C_2H_2^+$. Since this reaction is slightly exothermic, the absence of C_4H^+ as a secondary product of the reaction of $C_2H_2^+$ suggests that some activation energy is involved.

TABLE IV

COMPARISON OF PRIMARY AND SECONDARY MASS SPECTRA (BASED ON LARGEST OF PEAKS COMPARED)

Ion	Relative intensities: Primary from C_4H_4	Relative intensities: Sec. from $C_2H_2^+ + C_2H_2$	Ion	Relative intensities: Primary from C_4H_2	Relative intensities: Sec. from $C_2^+ + C_2H_2$
$C_4H_3^+$	100	100	C_4H^+	100	100
$C_4H_2^+$	83	81	C_4^+	24	45 ?
C_4H^+	13	6			

It is interesting also that the primary mass spectrum of C_4H_2 and the secondary spectrum of $C_2^+ + C_2H_2$ show approximate agreement for the C_4H^+ and C_4^+ ion intensities. The C_4^+ ion intensity was too small to permit a detailed study, but it seems reasonable that it might be formed from the reaction of C_2^+ ions.

As in the previous paper,[1] we measured the variation in ion intensities at a series of pressures while holding the repeller voltage constant and from this the rate constants for the various reactions at fixed voltage have been calculated by means of the equations (see ref. 1).

$$\frac{I_{S_j^+}}{I_{P^+} + \sum\limits_j I_{S_j^+}} = \frac{k_{S_j^+}}{\sum\limits_j k_{S_j^+}}\, k_1\,[\mathrm{M}]\,\tau_{P^+} \qquad (1)$$

$$\tau_{P^+} = \frac{1}{2A}\sqrt{B^2 + 2Ad_0} + \frac{d_0}{2B}\ln\frac{\sqrt{B^2 + 2Ad_0} + B}{\sqrt{B^2 + 2Ad_0} - B} \qquad (2)$$

$A = ev/m$

$B = \sqrt{8kT/\pi m}$

d_0 = distance from electron beam to the ion exit slit

v = ionization chamber field strength

In Table V, the rate constants are given at a field strength of 10 volts/cm. It is of interest that, as in the previous studies, the rate constants for the various reactions differ by a comparatively small amount.

TABLE V

RATE CONSTANTS FROM PRESSURE STUDIES (FIELD STRENGTH = 10 VOLTS/CM.)

	$\left(\frac{ks_j^+}{\Sigma ks_j^+}\right) k_1 \times 10^{10}$ (cc./molecule sec.)	$k_1 \times 10^{10}$ (cc./molecule sec.)
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$	5.0	
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$	3.9	
$C_2H_2^+ + C_2H_2 \rightarrow (C_4H_4^+)$		8.9
$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	7.3	7.3
$CH^+ + C_2H_2 \rightarrow C_3H_2^+ + H$	3.5	
$CH^+ + C_2H_2 \rightarrow C_3H^+ + H_2$	6.9	
$CH^+ + C_2H_2 \rightarrow (C_3H_3^+)$		10.4

The rate constants were also measured at different field strengths while holding the pressure constant. Table VI gives the average rate constants for the various reactions at several field strengths. In accordance with previous experience, all of these values tend to go through a maximum in the neighborhood of 8 to 20 volts per cm. Such discrepancies as are to be found between Tables V and VI are to be attributed to experimental error.

Equation (3) relates rate constant to reaction cross section, σ

$$k = f\sigma Q'/\bar{\tau} \qquad (3)$$

where

$$Q'/\bar{\tau} = \frac{A\bar{\tau}}{2} + \frac{B^2}{A\bar{\tau}}\left[\frac{247}{382} + \frac{1}{3}\ln\frac{2A\bar{\tau}}{\sqrt{B^2 + 3A^2\bar{\tau}^2}}\right] \qquad (4)$$

f is an efficiency factor, and other terms are defined above. Values of $f\sigma$ have been calculated from the measured rate constants and the results are given in Table VII.

In the previous paper we have shown that σ can be calculated from the equation

$$\sigma = \frac{e\pi\sqrt{\alpha}}{\sqrt{6kT + 2/3eVd_0}} \qquad (5)$$

where α is the polarizability. Values of σ have been calculated from equation 4 using $\alpha = 3.88 \times 10^{-24}$ from Landolt-Börnstein[12] and the results are given

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(11) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., in press.

(12) Landolt-Börnstein, "Zahlenwerte und Functionen, 6 Auflage, Atom und Molecular Physik," 3 Teil, Springer-Verlag, Berlin, 1950, p. 515.

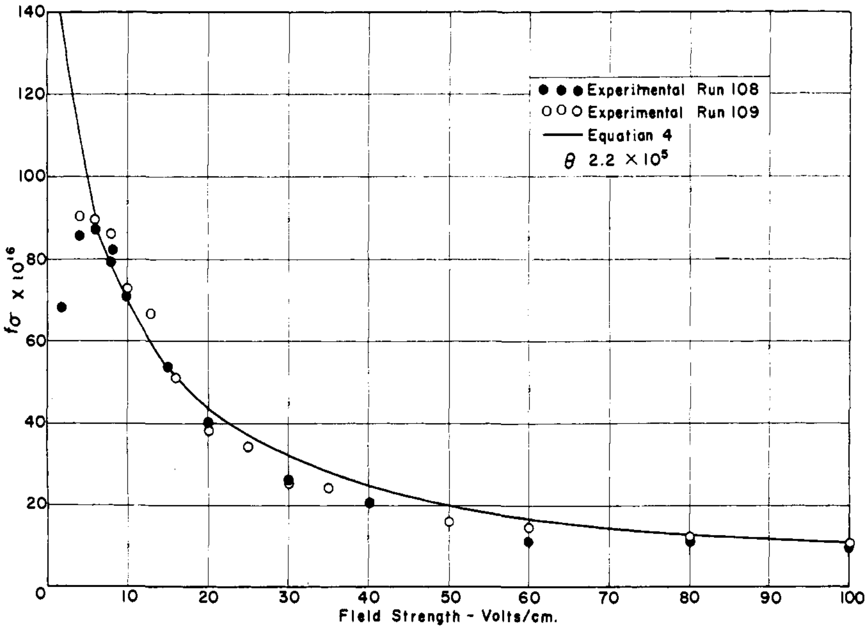

Fig. 1.—Typical plot of $f\sigma$ *vs.* field strength for $C_2H_2^+ + C_2H_2 \rightarrow [C_4H_4^+]$.

in Table VII. The agreement amongst the experimental cross sections for the various reactions is rather close as would be expected from theory.

As in the previous paper[1] rate constants and reaction cross sections for thermal speed ions were obtained by extrapolation from the more reliable higher field strength measurements. It was shown that the reaction cross section could be represented by

$$f\sigma = {}^1/_2\left(\frac{m_1(m_1 + m_2)}{m_2}\right)^{1/2} \frac{\theta e \pi \alpha^{1/2}}{\left(3kT + \frac{eVd_0}{3}\right)} \quad (6)$$

where the indices 1 and 2 refer to the ion and molecule, respectively, and with θ determined from the slope of a plot of $f\sigma$ *vs.* $1/(3kT + eVd_0/3)$. That equation 4 represents quite nicely the variation of $f\sigma$ with field strength is shown in Fig. 1. The rate constant for thermal speed ions was shown to be

$$k_{v=0} = \frac{\theta e}{6}\left(\frac{8\pi\alpha}{kT}\right)^{1/2}\left(\frac{m_\alpha + m_\beta}{m_\beta}\right)^{1/2} \quad (7)$$

where the index α always refers to the lighter reactant.

TABLE VI

REACTION RATE CONSTANTS AT VARIOUS FIELD STRENGTHS ($P_R \approx$ 5 MM.)

Reaction	$10^{10}\left(\frac{k_{sj}^+}{\Sigma k_{sj}^+}\right) k_1$, cc./molecule sec. at indicated V/d 100	60	40	20	10	8	6	2
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$	1.5	1.7	2.1	3.2	4.5	4.8	4.5	2.7
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$	1.7	1.7	2.0	2.7	3.7	3.9	3.6	2.2
$C_2H_2^+ + C_2H_2 \rightarrow (C_4H_4^+)$	3.2	3.4	4.1	5.9	8.2	8.7	8.1	4.9
$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	5.5	5.4	5.8	6.6	8.5	9.2	7.4	4.3
$CH^+ + C_2H_2 \rightarrow C_3H_2^+ + H$	1.8	2.1	2.4	3.2	3.0	2.6	2.0	1.1
$CH^+ + C_2H_2 \rightarrow C_3H^+ + H_2$	4.1	4.3	5.5	7.1	6.0	5.4	4.3	2.3
$CH^+ + C_2H_2 \rightarrow (C_3H_3^+)$	5.9	6.4	7.9	10.3	9.0	8.0	6.3	3.4

TABLE VII

CROSS SECTION, σ, IN CM.^{2} × 10^{16} AT INDICATED FIELD STRENGTH

Reaction		Field strength 100	60	40	20	10	8	6	2
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_4^+ \rightarrow$ Products	$f\sigma$	11	15	21	41	77	87	90	68
$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	$f\sigma$	18	22	29	45	68	85	84	55
$CH^+ + C_2H_2 \rightarrow C_3H_3^+ \rightarrow$ Products	$f\sigma$	14	19	28	50	58	55	49	34
Theoretical	σ	13	20	24	31	39	42	45	55

In Table VIII we list thermal reaction cross sections and rate constants calculated by our extrapolation method and rate constants calculated from the Eyring, Hirschfelder and Taylor[13] expression taking κ = 1.

Experimental

The experimental methods employed have been described

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(13) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936). See also Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 220 ff.

TABLE VIII

CROSS-SECTIONS AND RATE CONSTANTS FOR THERMAL REACTIONS

Reaction	Extrapolated experimental $f\sigma$ (298°K.) cm.^{2} × 10^{16}	Extrapolated experimental $k_{298°K.}$ (cm.^{3}/molecule·sec.) × 10^9	Theoretical (ref. 13) k (cm.^{3}/molecule·sec.) × 10^9
$C_2H_2^+ + C_2H_2 \rightarrow (C_4H_4^+)$	251	2.1	1.3
$C_2^+ + C_2H_2 \rightarrow C_4H^+ + H$	256	2.1	1.3
$CH^+ + C_2H_2 \rightarrow (C_3H_3^+)$	282	2.5	1.6

previously.[1] In studying reaction rates a Consolidated Electrodynamics Corporation (CEC) Model 21-620 cycloidal focusing mass spectrometer was used. In calibrating the ion source for pressure, the ionization cross section of acetylene was determined as $5.6_0 \times 10^{-16}$ cm.^{2} in reasonably good agreement with the value of 4.98×10^{-16} cm,^{2} reported by Massey and Burhop.[14] Appearance potentials were measured on a Westinghouse Type LV mass spectrometer. The acetylene used in these studies was commercial tank material obtained from Matheson Chemical Company and purified by repeated condensation at liquid nitrogen temperatures. The 1,3-butadiene was Phillips research grade having a stated purity of 99.51% and the 1-butyne was an API standard sample of 99.87% purity. Both were used without further purification. The vinylacetylene was obtained from the du Pont Company and was used without treatment since a mass spectrum indicated it to be of satisfactory purity.

Acknowledgment.—We wish to express our appreciation to Mr. B. L. Clark for his help in making the measurements and calculations.

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[14] H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p. 265.

BAYTOWN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Electronic and Vibrational States of the Nitrite Ion. I. Electronic States[1]

BY JEROME W. SIDMAN[2]

RECEIVED AUGUST 16, 1956

The lowest absorption transition of the nitrite ion has been studied in the crystalline state at 77°K. and at 4°K., using single crystals of $NaN^{14}O_2$ and $NaN^{15}O_2$ in polarized light. The corresponding fluorescence transition also has been studied. The spectra are sharp, and can be analyzed in considerable detail to yield vibrational and lattice frequencies for both the ground and excited electronic states. From the intensity dichroism and vibrational structure, it is concluded that the weak absorption transition of $NaN^{14}O_2$ with origin at 25977 cm.$^{-1}$ at 4°K. (25977 cm.$^{-1}$ for $NaN^{15}O_2$ at 4°K.) is allowed by symmetry and is polarized perpendicular to the plane of the NO_2^- ion ($^1B_2 \leftarrow {}^1A_1$). Comparisons with theory and with previous work are made wherever possible. The effect of environment on the electronic spectrum of NO_2^- is discussed. The NO_2^- spectra also are compared with the spectra of other 18-valence electron molecules, such as O_3, SO_2, HCO_2^-, ONCl, etc. The simplest LCAO-MO treatment appears to give a qualitatively correct description of the excited electronic states of NO_2^-

Introduction

Within the last few years, considerable progress has been made toward understanding the electronic spectra of polyatomic molecules. Although much attention has been given to large aromatic hydrocarbons, a survey of the literature reveals that relatively few triatomic molecular electronic spectra have been completely analyzed. The vapor spectra of triatomic molecules are sometimes sharp enough to permit analysis of the rotational fine structure, from which the transition moment direction and the geometry change can be deduced. However, even in such cases, there may be so many closely spaced bands present in the spectrum that the vibrational analysis is made difficult. Furthermore, if the molecule is very different from a symmetric top, the rotational analysis becomes quite difficult. In the cases in which the bands are broadened by predissociation, less information can be obtained.

The study of crystal and mixed crystal spectra has provided exact information about symmetry properties and vibrational structure of the electronic transitions of large, complex molecules. In this paper and in the following one, the results of such a study are reported for the lowest singlet-singlet electronic transition of the NO_2^- molecule-ion. Although it has been known since 1934 that the spectra of crystalline $NaNO_2$ and KNO_2 are sharp at low temperatures,[3] a complete analysis has not yet been given. The recent polarization studies of Trawick and Eberhardt[4] have provided additional information, which, together with the vibrational analysis presented in this work, lead to conclusions about the nature of the ground and lowest excited electronic states of this molecule. These results should also be applicable to other related molecules which possess the same number of valence electrons and similar geometry, and comparisons and predictions will therefore be made where possible.

Experimental

Mallinckrodt Analytical Reagent Grade $NaNO_2$ was further purified by recrystallization from water. Single crystals of suitable thickness were prepared readily by crystallization from molten $NaNO_2$ between quartz disks. The experimental arrangement used to record the absorption and fluorescence spectra of single crystals at low temperature has been described in a previous publication.[5] In this work, a tungsten filament lamp was the source for the absorption experiments, and a medium-pressure Hg arc with a Corning 5860 filter was used to excite the fluorescence of $NaNO_2$. All spectra were recorded on Kodak

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[1] This research was generously supported by the Office of Ordnance Research of the United States Army, under Contract DA-30-115 ORD-728 with the University of Rochester.

[2] Department of Theoretical Chemistry, Cambridge University, England. Post-doctoral fellow, 1955 to 1956, under a grant by the Shell Fellowship Committee to the Department of Chemistry of the University of Rochester.

[3] G. Rodloff, *Z. Physik*, **91**, 511 (1934).

[4] W. G. Trawick and W. H. Eberhardt, *J. Chem. Phys.*, **22**, 1462 (1954).

[5] J. W. Sidman, THIS JOURNAL, **78**, 4217 (1956).