[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL & REFINING COMPANY]

The Gaseous-Ion Sensitized Formation of Hydrogen Atoms

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Radiation-induced ethylene hydrogenation is sensitized by the addition of gases whose ionized forms are known to abstract hydrogen atoms from molecular hydrogen. The magnitude of the sensitization is proportional to the atomic number and inversely proportional to the average energy expended in sensitizer ion-pair formation. This latter observation is strong evidence of the actual occurrence of ion-molecule reactions in gas-phase radiation chemistry.

Introduction

Among the first and most easily observed gas-phase reactions between ions and molecules is the hydrogen atom transfer from the hydrogen molecule to an ionic reactant, *viz.*

$$X^+ + H_2 \longrightarrow XH^+ + H \tag{1}$$

in which X has been observed to be H_2, Ne, A, Kr, N_2, CO and H_2O[1-4]; most likely many other chemical species could serve as the ionic reactant. These reactions show the usual characteristic of observed ion-molecule reactions, in that they proceed with very high specific reaction rates—so high, in fact, that if the ionic species were to be formed under the conditions of a typical gas-phase radiolysis, it is difficult to conceive of reactions that might compete with their occurrence. Another common property of the reactions denoted by (1) is the formation of the same neutral species, namely, a hydrogen atom. These properties, when combined with the different characteristics of the various gases, X, with respect to absorption of energy from ionizing radiation, allow one to prepare radiolysis systems in which the rate of hydrogen atom formation depends only upon the nature of the gas that is added to hydrogen.

In a recent publication[5] it was shown that the addition of argon to irradiated hydrogen–ethylene mixtures sensitizes the selective hydrogenation of ethylene and that this is most reasonably interpreted as being due to an increase in the rate of formation of hydrogen atoms *via* (1). The purpose of this paper is to report further studies of such sensitization with other gases and to show how the magnitude of the sensitization provides strong evidence of the occurrence of (1) in gas-phase radiation chemistry.

Consider the irradiation of a mixture of hydrogen and a gas whose molecule-ion is known to react by (1). Neglecting excitation, the ions X^+ and H_2^+, formed in the primary act, will most probably react by (1). The resulting charged species, XH^+ and H_3^+, must be neutralized and, although the neutralization mechanism is not known, this process will necessarily lead to additional hydrogen atom formation. In this regard, the results of Biondi and Brown[6] indicate that neutralization of X^+ and H_2^+ cannot compete with (1) under the conditions usually employed in gas-phase radiation chemistry. Thus, the kinetically significant result of ionization of either X or H_2 is the formation of two hydrogen atoms (or perhaps four, as in the case of H_3^+ neutralization to 3H).

If we were to introduce ethylene into this system at concentrations such that it will not react significantly with H_2^+ or A^+ and will not absorb a large fraction of the radiation energy, the major chemical change taking place would be as a result of hydrogen atom attack on ethylene. The most likely reactions to occur at room temperature and under usual radiation conditions are now well established,[7] *viz.*

$$H + C_2H_4 \longrightarrow C_2H_5 \tag{2}$$

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \tag{3}$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \tag{4}$$

$$H + C_2H_5 \longrightarrow C_2H_6^* \tag{5}$$

$$C_2H_6^* \longrightarrow 2CH_3 \tag{6}$$

$$C_2H_6^* + M \longrightarrow C_2H_6 + M \tag{7}$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \tag{8}$$

It can be seen from (1)-(8) that the ultimate result of ionization of H_2 or X is the formation of ethane, propane and butane. Therefore, the increase in the rate of formation of ethane, propane and butane that occurs upon the addition of X to an irradiated system of ethylene and hydrogen is a measure of the energy of the ionizing radiation that goes into hydrogen atom formation.[5] Hence, if the hydrogen atom formation is due to occurrence of reactions of the type represented by (1), the amount of sensitization should be proportional to the rate of ionization of X. This, in turn, for all other factors held constant, should depend primarily upon the atomic number and ion-pair energetic requirements of the sensitizer.

Experimental

The radiation employed in this work was the electron beam from a 2-Mev. Van de Graaff electrostatic accelerator. In all experiments the accelerating voltage was maintained at 2.0 million v. and the electron beam current at approximately 5 μamp. The irradiation vessels and general irradiation procedures have been described previously.[8]

Phillips Research Grade ethylene, having a stated purity of 99.9+ mole %, was frozen out in liquid nitrogen and allowed to distill slowly into an evacuated storage bulb on the vacuum system, the middle third of the sample being collected. All other gases with the exception of helium and nitrogen were obtained from the Air Reduction Division of the Matheson Company and were used without further purification; helium and nitrogen were obtained from the Air Reduction Company of Houston and were used as received.

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(1) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

(2) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

(3) D. P. Stevenson, *J. Phys. Chem.*, **61**, 1953 (1957).

(4) F W. Lampe, F. H. Field and J. L. Franklin, THIS JOURNAL, **79**, 6132 (1957).

(5) F. W. Lampe, *Radiation Research*, **10**, 691 (1959).

(6) M. A. Biondi and S. C. Brown, *Phys. Rev.*, **76**, 1697 (1949).

(7) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corporation, New York, N. Y., 1954.

(8) F. W. Lampe, THIS JOURNAL, **79**, 1055 (1957).

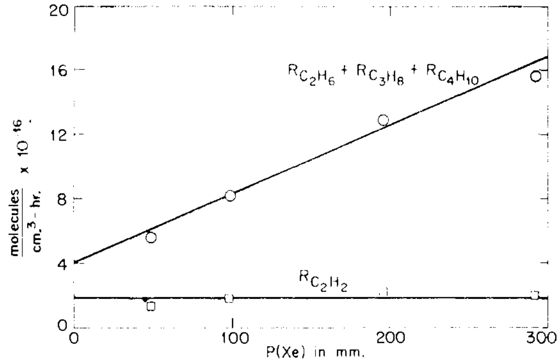

Fig. 1.—Hydrogen atom sensitization by xenon.

The analysis of products, which consisted essentially of acetylene, ethane, propane and *n*-butane, was carried out by vapor-liquid partition chromatography. The use of two columns (hexadecane and benzyl Cellosolve substrates on 40- to 60-mesh crushed firebrick) enabled complete separation and determination of all components, and, further, permitted internal checks between the two columns on the propane and acetylene analyses.

Generally speaking, the irradiations reported in this paper were of systems containing 300 mm. of hydrogen, 30 mm. of ethylene and varying amounts of sensitizer. Thus in all systems, the depletion of ethylene was necessarily very rapid and, since quantitative comparison of the sensitization effect must be made at identical ethylene concentrations, it was necessary to measure initial reaction rates. This was done by extrapolation of four or five apparent rates (amount of product divided by reaction time) to zero time. All reaction rates reported are initial rates unless otherwise stated.

Results and Discussion

In the previous work with argon[5] it was pointed out that the only significant products arising from irradiation of systems consisting of 30 mm. of ethylene, 300 mm. of hydrogen and varying amounts of sensitizer are acetylene, ethane, propane and *n*-butane. This is true also for all other sensitizers investigated. Other pertinent and general experimental facts are:

(1) The initial rate of acetylene formation is independent of sensitizer pressure.

(2) The initial rates of ethane, propane and butane formation increase with sensitizer pressure.

(3) The amounts of ethane and propane formed, relatively to that of butane, increase markedly with reaction time; the initial rates of formation of ethane and propane relative to that of butane increase with sensitizer pressure.

The experimental facts mentioned above are depicted graphically in Figs. 1 and 2. Figure 1 shows the sum of the initial rates of ethane, propane and butane formation and the initial rate of acetylene formation as functions of xenon pressure; this represents behavior that is typical of all sensitized systems investigated. The rise of the paraffinic formation rate with sensitizer is taken as evidence of the occurrence of (1)-(4), while the constancy of the acetylene formation rate is interpreted as indicating that acetylene arises only as a result of energy absorption by ethylene. Since it is difficult to conceive of acetylene being formed as a result of hydrogen atom attack on ethylene, this latter point is surely a reasonable interpretation. Incidentally, the reaction of xenon ion with hydrogen by (1) has not been observed directly as yet, but these results, as well as those of other investigators,[9] indicate that it does occur readily.

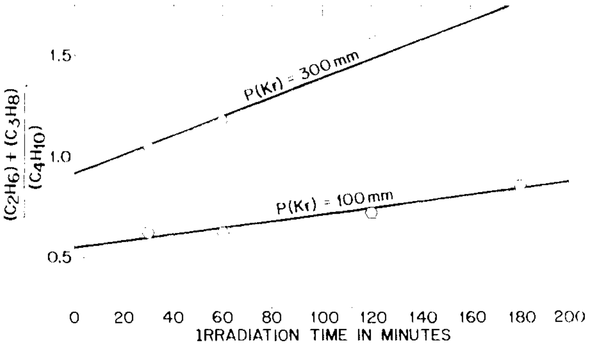

Fig. 2.—Effect of reaction time and krypton pressure on relative rates of product formation.

Fig. 2 shows the amounts of ethane and propane formed relative to butane as a function of reaction time for two pressures of krypton. The increase in these ratios with reaction time for both pressures of krypton is interpreted as being due to the rapid depletion of ethylene which makes more favorable the occurrence of (5)-(9) as opposed to (3) and (4). As ethylene is depleted (under our conditions of an essentially constant rate of formation of hydrogen atoms) the ratio of hydrogen atom concentration to ethyl radical concentration increases. Hence (5), which ultimately results in either ethane or propane formation, becomes more probable with increasing reaction time than (3) and (4) which form both ethane and butane—but, at room temperature, predominantly butane.[7] The slopes are in agreement with this hypothesis also, because at the higher pressure of sensitizer the ethylene is depleted more rapidly, leading to a more rapid rise in the ratio of ethane and propane to butane.

Similarly, the intercepts of Fig. 2, which represent the ratio of the sum of the initial rates of formation of ethane and propane to that of butane, are consistent with (5)-(8). Thus, as the sensitizer pressures are increased, all other factors held constant, the rate of hydrogen atom formation is increased. At constant ethylene pressures this also results in an increase in the ratio of hydrogen atom to ethyl radical concentration and the argument is as before. Therefore, both the effect of reaction time at constant sensitizer pressure and the effect of sensitizer pressure at constant ethylene pressure are consistent with the inclusion of (5)-(8) in the reaction scheme.

As a check on the possibility that the increasing paraffinic rates of formation and constant acetylene formation rate might be due to sensitizer-ethylene interaction, we carried out irradiations of ethylene and varying amounts of argon in the absence of hydrogen. The results are shown in Fig. 3 in which is plotted the ratio of the sum of the initial rates of ethane, propane and butane formation to the initial rate of acetylene formation *versus* the argon pressure. The constancy of the ratio in the absence of hydrogen and the increase in the ratio in the presence of a constant amount of hydrogen is

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(9) O. A. Shaeffer and S. O. Thompson, *Radiation Research*, **10**, 671 (1959).

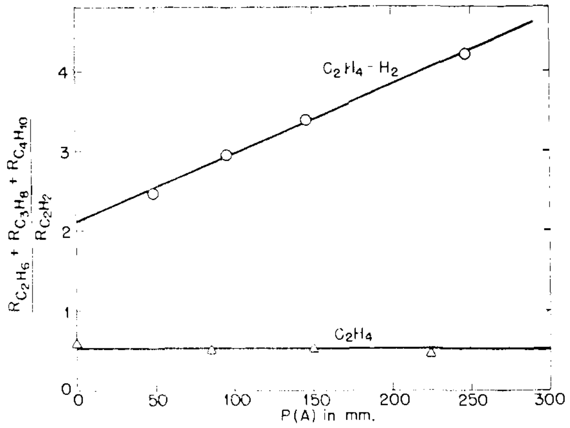

Fig. 3.—Effect of A on the radiolysis of C_2H_4 and C_2H_4–H_2 mixtures.

conclusive evidence that the effect is due to an argon–hydrogen interaction which we propose is that represented by (1) and which is to be expected for sensitizer-hydrogen systems known to undergo (1). Thus the experimental facts are at least qualitatively consistent with the occurrence of (1)-(8).

The behavior of krypton, neon and carbon monoxide as gaseous-ion sensitizers is shown in Fig. 4.

In considering the quantitative interpretation of this sensitization it is necessary to make certain assumptions and approximations. First, we assume that the formation of ethane, propane and butane in the radiolysis of pure ethylene does *not* occur *via* hydrogen atom reactions. If this assumption is valid, we can write our observed rates of formation of ethane, propane and butane as the sums of non-hydrogen atom reaction rates, R^0, and hydrogen atom reaction rates, ΔR; R^0 thus signifies formation of ethane, propane and butane, through direct absorption of energy by ethylene, while ΔR signifies formation of these products *via* hydrogen atoms produced by (1) and the neutralization of the ionic products of (1). Hence, denoting initial rates of formation by R, we have

$$R_{C_2H_6} = R^0{}_{C_2H_6} + \Delta R_{C_2H_6} \tag{9}$$

$$R_{C_3H_8} = R^0{}_{C_3H_8} + \Delta R_{C_3H_8} \tag{10}$$

$$R_{C_4H_{10}} = R^0{}_{C_4H_{10}} + \Delta R_{C_4H_{10}} \tag{11}$$

Secondly, we assume that all hydrogen atoms react by the sequence (2)-(8). Then, from the stoichiometry of these reactions, we can write for the rate of formation of hydrogen atoms

$$R_H = 2\ \Delta R_{C_2H_6} + 2\ \Delta R_{C_3H_8} + 2\ \Delta R_{C_4H_{10}} \tag{12}$$

Thirdly, we assume that (1) followed by neutralization of XH^+ and H_3^+ represents the consequences of energy absorption by hydrogen and the added sensitizer and further that neutralization of H_3^+ results in one hydrogen atom. Since H_2^+ and X^+ result in the formation of two hydrogen atoms, we have

$$R_H = \frac{2Q_{H_2}}{W_{H_2}} + \frac{2Q_x}{W_x} \tag{13}$$

in which Q is the rate of energy absorption by the gas denoted by subscript and W is the average energy expended in forming an ion-pair in the gas being considered.

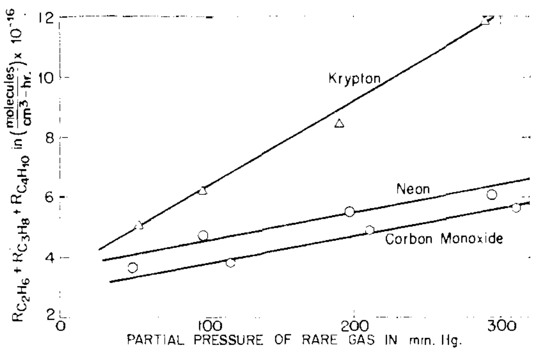

Fig. 4.—Hydrogen atom sensitization by krypton, neon and carbon monoxide.

According to Bethe,[10] the loss of energy per unit length of path of the primary electron can be written

$$-\frac{dT}{dx} = \frac{2\pi e^4 NZ}{mv^2}\left[2 \ln\left(\frac{2mv^2}{\bar{E}}\right) - \ln(1 - \beta^2) - \beta^2\right] \tag{14}$$

in which N is the number of atoms of atomic number Z per cm.^{3}, v is the velocity of the primary electrons, e and m are the charge and mass of the electron, respectively, β is the ratio of the velocity of the electrons to the velocity of light and $\bar{E}$ is the mean excitation potential of the atom; the term in brackets is usually known as the stopping number of the medium for electrons. Denoting the bracketed term by B, recognizing that v is approximately constant (for gaseous systems, such as considered here, the primary particle loses very little energy) and remembering that all irradiation conditions of current and voltage are held constant, we can write for the rate of absorption of energy

$$Q_x = \alpha Z_x P_x B_x \tag{15}$$

where α is a constant, P is the partial pressure of x and the other terms are as before. Combining (12), (13) and (15) and remembering that P_{H_2} is also constant, we get

$$\Delta R_{C_2H_6} + \Delta R_{C_3H_8} + \Delta R_{C_4H_{10}} = A' + \frac{\alpha Z_x B_x P_x}{W_x} \tag{16}$$

where the constant A' represents the increase in paraffinic rate due to (1) for $X = H_2$. Upon the summation of (9)-(11) and substitution of (16), we get for the observed rate of paraffinic product formation

$$R_{C_2H_6} + R_{C_3H_8} + R_{C_4H_{10}} = A + \frac{\alpha Z_x B_x P_x}{W_x} \tag{17}$$

In (17), the constant A represents the rate of such product formation in the presence of constant amounts of ethylene and hydrogen. As the extent of any radiation-induced interaction between these species, in addition to (1)-(8), is unknown, it is not possible to separate the constant A into two energy absorption terms, one for ethylene and the other for hydrogen.

From (17) it can be seen that a plot of the sum of the observed rates of formation of ethane, propane and butane *versus* sensitizer pressure should be linear with constant intercept A and slope

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(10) H. Bethe, "*Handbuch der Physik,*" Vol. XXIV, 1933 p. 273; see also F. W. Spiers, *Discussions Faraday Soc.*, **12**, 13 (1952).

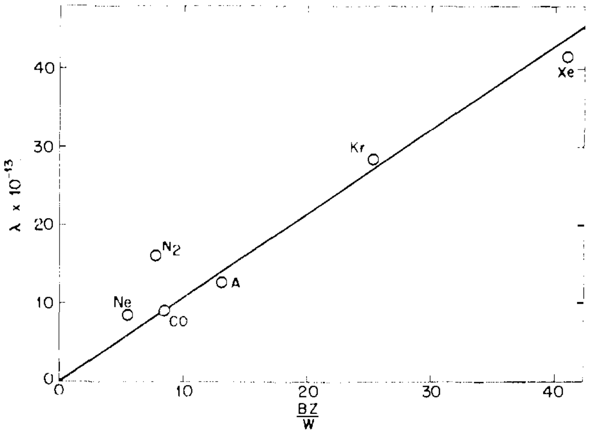

Fig. 5.—Gaseous ion sensitization of hydrogen atom reactions.

$\frac{\alpha ZB}{W}$. The plots are shown in Figs. 1, 3 and 4, where it can be seen that they are indeed linear within experimental error. In order to compare numerically the argon sensitization shown in Fig. 3 with that of the other gases (Figs. 1 and 4) it is necessary to multiply the slope of Fig. 3 by the rate of acetylene formation (1.57×10^{16} molecules/cm.^{3} hr.). The average intercept obtained for Ne, CO, A, Kr and Xe sensitization is $3.4 \pm 0.3 \times 10^{16}$ molecules/cm.^{3} hr., which is a satisfactorily constant value. A low value (2×10^{16}) was obtained for this intercept in a few experiments with N_2 as sensitizer.

According to our hypothesis the degree of sensitization, or slopes of the plots of Figs. 1, 3 and 4, should be proportional to $\frac{BZ}{W}$. In Fig. 5 is shown the least square slopes of Figs. 1, 3 and 4, plotted as a function of calculated values of the quantity $\frac{BZ}{W}$. Values of B were calculated using (14) and the values of $\bar{E}$ tabulated by Mano[11]; values of W were obtained from the recent paper by Weiss and Bernstein[12]; W for carbon monoxide was estimated by assuming that the ratio of W to ionization potential for carbon monoxide was equal to that same quantity for nitrogen.

The agreement with proportionality shown in Fig. 5 for neon, carbon monoxide, argon, krypton and xenon is very good. The value for nitrogen, however, is high. It is conceivable that some additional chemical reactions following neutralization of N_2H^+ are responsible for this divergence, but it seems more likely that it is a result of a large experimental error in the analyses of one set of experiments. It has been mentioned that the intercept for the nitrogen sensitized system derived from a few measurements was low. If this intercept is set equal to the value of 3.4×10^{16} (the average value found for the other five sensitizers), the average slope then obtained for nitrogen from 3 scattered points is in fairly good agreement with the line drawn in Fig. 5. Helium exhibited some sensitization, indicating the occurrence of (1), but due to our experimental uncertainties in initial hydrogen and helium pressures and the possible breakdown, for low degrees of sensitization, of our assumption that the observed rate can be written as the sum of two independent rates, we do not believe these results to be much more than qualitative.

As a further test of the validity of the treatment, the proportionality constant α, which is the slope of Fig. 5, can be used to compute an experimental value of the quantity $\frac{2\pi e^4}{mv^2}$ for comparison with the actual value. That these quantities are related easily can be seen by reference to (14) and (15). The relationship for systems such as this in which $\frac{dT}{dx}$ is essentially constant is easily shown to be

$$\frac{2\pi e^4}{mv^2} = \frac{Ve}{\bar{I}d}\alpha \qquad (18)$$

in which $\bar{I}$ is the average primary electron current traversing the gas, e is the electronic charge, V is the gas volume, d is the path length and the other terms are as before. In all experiments we employed an incident beam current of 5.0 microamperes but because of scattering in the window, the effective primary electron current in the vessel was much less. We define the effective primary electron current as the number of electrons per second traversing cross-sectional area of the cylindrical reaction vessel, averaged over the total length of the vessel. The averaging is carried out as follows: when the divergent primary electron beam area is less than the vessel cross-sectional area, we define I as constant and equal to I (incident); when the beam area is greater than the reaction vessel cross-section, we define I at any point in the path as the product of the incident current by the ratio of the cross-sectional area of the vessel to the area of the beam. We estimate the beam divergence by assuming that small-angle coulomb scattering, such as treated by Fermi[13] for a statistical number of encounters, occurs in the Pyrex window and is superimposed upon the divergence of 7° that we have observed for a five microampere incident beam. Considering Pyrex to be composed of SiO_2 that behaves cumulatively as an element of atomic number 10, we arrive at a total beam divergence of 20°. Then averaging as indicated above leads to an effective primary electron current of 0.42 microampere; d is 60 cm.

From the measured slope of Fig. 5 (put into the appropriate units of the c.g.s. system), the values of I and d mentioned above and the reactor volume of 250 cm.^{3}, we get an experimental value for $\frac{2\pi e^4}{mv^2}$ of 2.4×10^{-31} erg.cm.^{2}. This is to be compared with the actual value of 4.4×10^{-31} erg.cm.^{2} computed for 1.7 mev. electrons (an energy loss in the Pyrex window of 0.3 mev. per electron occurs). Considering the uncertainties in $\bar{I}$, this agreement is quite satisfactory and is considered to be confirmatory evidence of the basic correctness of the treatment.

We submit that the proportionality and agreement of the slope of Fig. 5 with theory is

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(11) G. Mano, *J. phys. radium*, **5**, 628 (1934).

(12) J. Weiss and W. Bernstein, *Phys. Rev.*, **103**, 1253 (1956).

(13) E. Fermi, "Nuclear Physics," University of Chicago Press, Chicago, Ill., 1950, p. 37.

strong evidence of the occurrence of (1) in this gas phase radiolysis system. Since there is nothing unique about the reaction rate of (1), we conclude that these results support the view that ion–molecule reactions are of general importance in gas-phase radiation chemistry.

An alternate possibility to the gaseous-ion sensitization is excited atom sensitization, because the quantity $\frac{BZ}{W}$ should also be proportional to the rate of formation of excited species. Thus the mode of hydrogen atom formation might be

$$X^* + H_2 \longrightarrow X + 2H \qquad (19)$$

It is not possible to refute this completely, but it would seem that if (19) were occurring to any great extent, then as the sensitizer pressure was increased, the probability of deactivation by $X^* + X$ collisions would become more probable than (19). This would result in a non-linearity of $R_{C_2H_6} + R_{C_3H_8} + R_{C_4H_{10}}$ with sensitizer pressure, as has been observed for the rate of ethylene consumption as a function of argon pressure in studies of the ethylene–argon systems.[5] The corresponding dissipation of charge in $X^+ + X$ collisions is not possible.

It is not at present possible to rule out the protonation of ethylene by XH^+, *viz.*

$$XH^+ + C_2H_4 \longrightarrow X + C_2H_5^+ \qquad (20)$$

However, the formation of $C_2H_5^+$ would not be expected to lead to the same products as hydrogen atom formation in the presence of ethylene, unless every $C_2H_5^+$ was neutralized to $C_2H_4 + H$. This latter event would, of course, be kinetically indistinguishable from (1) followed by neutralization of XH^+ and H_3^+. The reaction

$$XH^+ + C_2H_4 \longrightarrow X^+ + C_2H_5 \qquad (21)$$

can be ruled out on energetic grounds.

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BAYTOWN, TEXAS

[CONTRIBUTION FROM THE MASS SPECTROMETRY SECTION, NATIONAL BUREAU OF STANDARDS]

Electron Impact Study of the Cyanogen Halides[1]

BY JOHN T. HERRON AND VERNON H. DIBELER

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Mass spectra and appearance potentials are reported for the principal ions of cyanogen chloride, bromide and iodide. Using these data, the following thermochemical values have been computed: $\Delta H_f CN = 89 \pm 2$ kcal./mole; $\Delta H_f CN^- = 15 \pm 4$ kcal./mole, $E.A.(CN) = 74 \pm 4$ kcal./mole.

Introduction

The cyanogen halides form an interesting series of compounds bearing certain resemblances to mixed halogen compounds in the ease with which they form negative ions. Furthermore, they provide a homologous series containing the CN group, of which the heat of formation, ionization potential and electron affinity are of interest for numerous thermochemical applications.

Recent studies of the ionization–dissociation processes in cyanogen, C_2N_2, have been reported by McDowell and Warren,[2] Kandel,[3] and by Stevenson.[4] The only published appearance potential for the cyanogen halides is also due to Stevenson,[4] but is limited to the Cl^+ ion of cyanogen chloride. As some uncertainties remain in the interpretation of the dissociation process in cyanogen chloride and cyanogen, further work including the halogenated series seems to be warranted. An additional incentive is the reliable determination of heats of formation of cyanogen chloride, bromide and iodide by Lord and Woolf.[5]

Experimental

The mass spectrometer was essentially the conventional 60° sector-type instrument. Magnetic scanning was used at a constant ion accelerating potential of 5000 volts. Mass spectra were obtained using 70 v. electrons.

Usual procedures for appearance potential studies were employed. That is, the anode of the ion source was operated at about the same potential as the ionization chamber. The ion repeller was biased 3 v. positive with respect to the ionization chamber when studying positive ions and 1.5 v. negative for negative ions. The temperature of the ion source was about 250°.

Appearance potential measurements were made by varying the electron energy by means of a Shallcross decade potentiometer across a carefully regulated and measured 100.0 v. power supply. The electron accelerating voltage was usually varied in 0.1 v. steps.

The electron energy scale for positive ions was calibrated by means of argon, using the spectroscopic ionization potential of 15.76 e.v.[6]

In the case of negative ions, no single calibration point was found acceptable over the required energy scale. It was found necessary to separate negative ions into two energy ranges, *i.e.*, 0 to 2 ev. and above 2 ev. Furthermore each range required an optimum setting of source magnet and emission control to attain stable operation.

Ion currents were measured with a 10-stage electron multiplier, vibrating reed electrometer and recording potentiometer. Under favorable conditions, the minimum detectable current was estimated to be 10^{-18} amp.

Table I lists the negative ions used as calibration points. Positive ion appearance potentials were evaluated by normalizing the slopes of the unknown and reference curves, plotting on a semi-log scale and determining the voltage in-

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[1] This research was performed as part of the National Bureau of Standards' Free Radical Research Program supported by the Department of the Army.

[2] C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

[3] R. J. Kandel, *J. Chem. Phys.*, **22**, 1496 (1954).

[4] D. P. Stevenson, *ibid.*, **18**, 1347 (1950).

[5] G. Lord and A. A. Woolf, *J. Chem. Soc.*, 2546 (1954).

[6] C. E. Moore, *Natl. Bur. Standards Circular*, 467 (1949).