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The Reactions of Radicals Produced by the Action of Sodium on Alkyl Iodides

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The products of the reactions of sodium vapor with methyl and ethyl iodide vapors have been analyzed. It has been found that in the reaction with methyl iodide the principal product is ethane, but considerable amounts of methane, ethylene, and hydrogen are also formed. With ethyl iodide the principal product was butane, with lesser amounts of ethane, ethylene, methane, and hydrogen. It was also noted that in the latter system considerable amounts of propane appeared which could be accounted for as a pyrolysis product of the butane formed. The results have been compared with those obtained by others with similar systems and with the results obtained in the photolyses of mercury dimethyl and mercury diethyl. It is concluded that at low temperatures the dominant reaction for both ethyl and methyl radicals is for two to combine to form a saturated hydrocarbon. At higher temperatures, disproportionation reactions and reactions of the radicals with other molecules must be taken into account and eventually become the dominant reactions.

OR many years it has been a common practice to assume the existence of various free radicals as intermediates in the thermal or photochemical reactions involving organic molecules. In setting up mechanisms for these reactions, various possibilities have been suggested for the formation of the products from these radicals, but, as a rule, it has not been possible to make a unique decision between two or more methods of achieving the ultimate result. Furthermore, we find such anomalies as the assumption by one author that methyl radicals react to form ethane, whereas another assumes that they form methane and a methylene radical. In this paper we wish to report the results on the reactions of methyl and ethyl radicals prepared under conditions such that the possibility of complicating side reactions has been reduced to a minimum.

The radicals were prepared by the action of sodium vapor on the vapor of the appropriate alkyl iodide. Polanyi¹ has studied these reactions extensively in the presence of a carrier gas and has concluded that reaction occurs at about every collision between a sodium atom and an alkyl iodide molecule. He has not investigated the subsequent reactions of the radicals. Saffer and Davis² studied the products produced by heating liquid sodium in the presence of about 200-mm pressure of various alkyl iodides. They believed that the reaction occurred in the gas phase but did not vary the experimental conditions or in any way exclude the possibility that reactions could occur at the surface of the sodium. Bawn and Tipper³ have studied the products produced when sodium vapor reacts with ethyl or methyl iodide in a stream of hydrogen or nitrogen gas at temperatures of 300 to 363°C. Their results are related to ours and will be discussed in detail later.

Most thermal and photochemical reactions in which methyl or ethyl radicals have been assumed as intermediates offer too many possibilities for these radicals to

react with other molecules for the results to be comparable with those to be presented in this paper. However, there are some simple systems which are comparable. The photolysis of methyl iodide has been studied by Schultz and Taylor⁴ and also by West and Schlessinger.⁵ The latter authors have also studied the photolysis of ethyl iodide. The photolysis of dimethyl mercury has been studied by Gomer and Noyes,⁶ Phibbs and Darwent,7 and Cunningham and Taylor.8 The photolysis of diethyl mercury has been studied by Moore and Taylor.⁹ In all of these cases, the results can be related to those presented in this paper; therefore, they will be discussed in detail later. In these photochemical studies the number of radicals formed has been quite small compared to the total number of molecules present. The experiments which we are about to describe were designed to make the number of radicals present large compared to the number of other molecules and thus greatly increase the probability of radicals reacting with each other rather than with some other molecule.

APPARATUS

Since radicals probably react at a glass surface, a five liter flask was used to enclose our reaction system and thus favor, as much as possible, the occurrence of homogeneous reactions. Figure 1 illustrates the experimental arrangement. D is the flask with the tube Gextending from the ground glass joint H, through the neck, to the center of the flask. G is about 4.5 cm in diameter and is connected at the top by a Dewar seal to the tube S, which is concentric to it. G and S differ sufficiently in diameter to permit the insertion of the single chromel heater winding, I, covered with baked

¹ For example, see H. von Hartel and M. Polanyi, Z. physik. Chem. **B11**, 97 (1930).

² A. Saffer and T. W. Davis, J. Am. Chem. Soc. 64, 2039 (1942). ³ C. E. H. Bawn and C. F. H. Tipper, Faraday Soc. Discussions 2, 104 (1947).

⁴ R. D. Schultz and H. A. Taylor, J. Chem. Phys. 18, 194 (1950). ⁵ W. West and L. Schlessinger, J. Am. Chem. Soc. 60, 961

^{(1938).} ⁶ R. Gomer and W. A. Noyes, Jr., J. Am. Chem. Soc. 71, 3390

⁷ M. K. Phibbs and B. deB. Darwent, Trans. Faraday Soc. 45, 541 (1949).

⁸ J. P. Cunningham and H. S. Taylor, J. Chem. Phys. 6, 359 (1938)

⁹ W. J. Moore and H. A. Taylor, J. Chem. Phys. 8, 396 (1940).

out wet asbestos paper. The current through the heater is controlled by a variac. At the bottom of S is a small thermocouple well. J is a cylindrical bulb containing the sodium; it is concentric to G and S but not attached to either. The bottom of J is shaped to fit over the thermocouple well in S, and the top is drawn down to form a jet of about 5 mm internal diameter.

At the top of the bulb D is the tube C in which the rod B can be slid up and down by means of a magnet operating on the piece of soft iron A. At the lower end of B is a cover which fits over the opening in the sodium tube J. F is a thermocouple well which was placed in the exit tube T in order to measure the temperature at the surface of the flask.

It was desired to calculate a material balance for the reactions; hence, it was necessary to know the amount of iodide introduced in each experiment. The iodide was degassed by successive freezing and thawing and pumping off the liberated gas while the iodide was frozen. When a sample was not being taken, the reserve of the iodide was kept frozen. To introduce a sample into the reaction vessel, the reservoir was brought to 0°C by surrounding it with ice and water. The iodide was allowed to vaporize into a doser bulb, volume not greater than 100 ml, until the equilibrium vapor pressure at 0° was attained. Then the doser bulb was shut off from the reservoir, and the vapor expanded into the reaction vessel D. With ethyl iodide, the vapor pressure was so low at 0° that, in order to obtain enough vapor for the higher pressure runs, it was necessary to collect two or more doses by freezing them out in a side tube and then, finally, vaporizing the entire amount into the reaction vessel.

The apparatus used for handling the reaction products differed slightly for methyl and ethyl iodides. It was not necessary to fractionate the products of the methyl



iodide reaction (excess sodium was always used so there was no residual methyl iodide); hence, after the reaction was completed, the products were pumped from the reaction bulb into a storage bulb by means of a mercury vapor pump. This process was facilitated by cooling a side tube on the storage bulb during the pumping, thus condensing some of the products. After the transfer was complete, the condensable products were vaporized and mixed with the others before they were transferred to the analytical apparatus.

The arrangement used to fractionate the products from the ethyl iodide reaction is shown in Fig. 2. The products first passed through the trap I, which was cooled with liquid nitrogen. The noncondensable portion was collected and analyzed on the assumption that it contained only hydrogen and methane. The method used for the separation of the condensable products was essentially the same as that used by Saffer and Davis, except that instead of using freezing mixtures we used the arrangement shown. The trap O is surrounded by a chromel heating element the leads for which pass through the seal M in the tube J. J is concentric with O. The air pressure between O and J can be varied by opening the stopcock K to the atmosphere or by connecting it to a mechanical vacuum pump. L is a thermocouple well so that the temperature of the inner trap O can be measured. The condensable products were transferred from I to O by surrounding J with liquid nitrogen and opening K to the atmosphere. When the thermocouple indicated that O was approximately at liquid nitrogen temperature, I was warmed until the products had passed over to O. The temperature of Owas then varied by reducing the pressure in J and sending a small current through the chromel wire heater. The products which vaporized with O held at 135°K were analyzed on the assumption that they were only methane, ethane, and ethylene. The next fraction was taken off at 195°K and analyzed as a mixture of ethane, ethylene, propane, and propylene. The remainder was treated as a mixture of propane, propylene, butane, and butylene.

GAS ANALYSIS

The gas mixtures were analyzed by means of an apparatus in which the essential features of the low pressure arrangement designed by C. H. Prescott¹⁰ were utilized. Certain additional units were added to make the equipment suitable for the analysis of the gases obtained in our experiments. With this arrangement, a sample of the gases to be analyzed was measured in a gas burette and mixed with oxygen or whatever other gas was needed as a reagent in the analytical procedure. The usual practice was to run a combustion and determinations of hydrogen and olefins.

For combustion, the sample was mixed with excess oxygen and compressed into a small tube fitted with a

¹⁰ C. H. Prescott, Jr., J. Am. Chem. Soc. 50, 3237 (1928).

platinum filament. This filament was welded to the ends of some heavy platinum leads which in turn were silver soldered to the tungsten leads which were sealed through the glass. The filament was sufficiently far removed from the silver solder and tungsten that neither of them would be heated enough to cause any oxidation during the course of a combustion. In order to insure complete combustion, the filament was heated for ten minutes, then the gas was returned to the gas burette and the volume redetermined. Next, this gas was passed through a coil immersed in a dry ice-acetone bath to remove water vapor, and the volume was measured again. Finally, the gas was passed through a coil immersed in liquid nitrogen to freeze out carbon dioxide and the volume remeasured. In this manner the number of moles of carbon dioxide formed per mole of sample and the number of moles of oxygen required per mole of sample were determined.

Hydrogen and the olefins could be determined by catalytic hydrogenation. The catalyst was prepared by saturating shredded asbestos with molten nickel nitrate hexahydrate. Heating with either a Bunsen burner or a gas-oxygen hand torch dehydrated and decomposed the nitrate, leaving nickel oxide on the asbestos. The oxide coated asbestos was placed in a Pyrex tube in an electric heater, and hydrogen passed through it overnight. The asbestos was then transferred to a small tube on the gas analysis apparatus. Since, in this last step the catalyst was exposed to air, a final reduction and activation was carried out after it was installed in the apparatus. For this purpose, a small heater was placed around the tube and a considerable amount of hydrogen admitted. After fifteen or twenty minutes of heating, the catalyst was allowed to cool, and the hydrogen was pumped off. Activation was always necessary after any exposure of the catalyst to air or oxygen. It was also found that mercury poisoned the catalyst permanently. Frequent tests of the activity of the catalyst were made by running blank hydrogenations of ethylene by hydrogen.

The olefinic content of a sample was determined by mixing it with a known excess volume of hydrogen and exposing the mixture to the action of the catalyst for ten minutes. The decrease in volume measured the number of moles of olefin present. Correspondingly, if an excess of ethylene was added to a different sample and exposed to the catalyst, the decrease in volume measured the amount of hydrogen present.

MATERIALS

The methyl and ethyl iodides were washed to remove iodine and other impurities and dried with phosphorus pentoxide. Then they were fractionated in a Vigreux column and the middle fraction, which boiled within $\pm 0.5^{\circ}$ of the accepted boiling point, was kept for use. After distillation the iodides were stored in the dark over a few drops of mercury.

The sodium was cut from large pieces of the laboratory supply and melted under a vacuum. While in the



molten state, it was allowed to flow through a constriction into a tube of the form shown at J in Fig. 1. It was heated until the evolution of gas appeared to be complete, then the tube was sealed off at the constriction. Later, this tube was cut off in the constricted part so as to leave it in the condition described in connection with Fig. 1. Air entered at this stage but only for a brief interval, since the tube was immediately placed in the indicated position in the reaction assembly and the system evacuated. The sodium was degassed further by heating it in place in the reaction system. Even with these precautions, it was found impossible to completely eliminate the evolution of gas from the molten metal, and this fact prevented us from making runs at very low pressures.

EXPERIMENTAL PROCEDURE AND RESULTS

The general procedure was to heat the sodium until it reached a certain desired temperature, which was always at least 400°C. Then the dose of iodide needed to give the desired pressure was introduced. Next, the cover E was lifted; the sodium vapor came out as a small sphere, which expanded rapidly to fill the flask. The course of the sodium vapor was followed by observing the fluorescence which was excited by illuminating the reaction vessel with the light of a sodium vapor lamp. The reaction was complete in ten to fifteen seconds or less. When excess sodium was present, the cover was replaced on L and the products pumped out as rapidly and completely as possible. It was found necessary to flame the reaction bulb after the reaction in order to obtain all of the gaseous products.

Some sodium leaked out from under the cover, E, and condensed on the walls of the large bulb during the preliminary heating. This fact did not lead to any complication, since the temperature of the wall never exceeded 150°C. At this temperature no appreciable reaction occurs between the methyl iodide and the sodium on the wall in the time required for an experiment.

The experiments with methyl iodide were carried out under three sets of conditions, as indicated in Table I.

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TABLE I. Products obtained from the reaction of sodium with methyl iodide.

Moles of	product/mole	dide used	Percent yield		
H ₂	CH4	C2H4	C2H6	H•	C*
I. 1	Methyl iodi	de pressure:	=0.47 mm; s	odium at 420	°C.
0.025	0.187	0.094	0.312	101	100
0.070	0.185	0.070	0.312	101	95
0.040	0.247	0.040	0.297	100	91.5
0.070	0.191	0.077	0.300	100	94.5
0.055	0.286	0.048	0.293	104	96.5
II.	Methyl iodi	ide pressure	= 2.35 mm;	sodium at 48	5°C.
0.036	0.271	0.079	0.217	92	86
0.020	0.354	0.049	0.228	101	91
0.007	0.541	0.015	0.180	104	93
0.000	0.450	0.028	0.188	101	88
III. N	fethyl iodid	e pressure=	2.35 mm; so	dium at 450-	460°C.
0.000	0.250	0.033	0.332	96.5	91
0.012	0.292	0.021	0.284	99.5	90
0.012	0.340	0.030	0.234	97	87
0.006	0.218	0.028	0 322	08	02

• Percent yield of hydrogen is the number of gram atoms of hydrogen contained in the gaseous products, divided by the number of gram atoms of hydrogen in the methyl iodide used, and multiplied by 100. Percent yield of carbon is calculated in a similar manner.

Under the sets of conditions designated as I and III, the course of the reaction, as manifested by the sodium fluorescence, was essentially the same. Under these conditions, when the cover E was lifted, a sphere of sodium vapor formed, remained at constant diameter for a brief interval, and then expanded to fill the entire vessel. The reaction was complete in from ten to fifteen seconds. In the set of runs designated as II, the reaction was complete in about one second. As soon as the reaction was complete the products were pumped out of the reaction vessel and the total volume of the gases measured in a gas buret. Combustions and hydrogenations were carried out as previously described, and the

TABLE II. Products obtained from the reaction of sodium with ethyl iodide.

Moles of product/moles of ethyl iodide used									
H2	CH₄	C ₂ H ₆	C ₂ H ₄	C ₈ H ₈	C4H10	+C4H10	H	С	
I.	Pressu	re of et	hyl iodi	de=0.6	9 mm;	sodium a	t 380°C		
0.049	0.013	0.137	0.069	0.232	0.117	0.349	85.5	79.5	
0.072	0.013	0.168	0.095	0.000	0.352	0.352	102	97	
0.058	0.016	0.123	0.143	0.000	0.350	0.350	99.5	97	
not	det.	0.166	0.040	0.034	0.301	0.335	not	det.	
II	. Press	ure of e	thyl iod	ide = 2.7	78 mm;	sodium a	at 445°(C.	
0.066	0.024	0.13	0.07	0.075	0.247	0.322	87.5	82	
0.049	0.005	0.157	0.016	0.12	0.199	0.319	81.4	75.4	
0.080	0.007	0.155	0.021	0.00	0.313	0.313	86.9	80.8	
0.056	0.019	0.142	0.022	0.124	0.230	0.354	88.5	82	
0.043	0.007	0.158	0.049	0.000	0.318	0.318	90.6	85	
III. I	Pressure	of ethy	yl iodid	e=2.78	mm; so	dium at	460-47	0°C.	
0.07	0.008	0.217	0.029	0.046	0.184	0.230	76	69	
0.055	0.004	0.151	0.085	0.000	0.250	0.250	77.5	73.8	
0.097	0.003	0.108	0.108	0.111	0.181	0.292	80	75	
IV. Pr	essure	of ethyl	liodide	= 2.78 1	nm; soo	lium at a	ibout 4	90°C.	
0.086	0.032	0.095	0.185	0.263	0.077	0.340	91	85	

composition of the gas was calculated from the data thus obtained.

The general procedure was the same in the experiments with ethyl iodide. The specific differences in experimental conditions are indicated, along with the results, in Table II. The products were fractionated and analyzed as already described. One noticeable difference from the methyl iodide experiments was that, in this case, chemiluminescence accompanied the reaction. In the fastest reactions, a white luminescence appeared as a long ellipsoidal flame above the jet for a brief interval after the cover was lifted. Otherwise, the color was the characteristic sodium yellow of lower intensity, decreasing in intensity as the reaction proceeded. The products were fractionated, as previously described, and the compositions of the various fractions were determined by measuring the total volume, the numbers of moles of carbon dioxide formed, and the numbers of moles of oxygen used in combustion.

DISCUSSION OF RESULTS

It is apparent from a survey of the results listed in Table I that the principal products obtained in the experiments with methyl iodide are methane and ethane. Furthermore, the material balance shows that no major product has been missed. These results are in qualitative agreement with the results of Saffer and Davis² and those of Bawn and Tipper,3 although both of them reported relatively larger percentages of methane. The temperatures in our experiments were not as well defined as those in the experiments of Bawn and Tipper, since we did not use a carrier gas. However, even in their experiments there is some question as to the actual temperature in the reaction zone. The reactions of alkyl iodides with sodium vapor are exothermic by a considerable number of kilocalories, and this energy must be distributed between the alkyl radical and sodium iodide molecule which are produced. An appreciable amount of time is required to reduce the energies of these "hot" molecules to a normal thermal distribution. It was shown by Berry and Rollefson¹¹ that fast moving sodium atoms require many collisions to reduce their speeds to values characteristic of the temperature of the gas in which they are moving. The effective temperature in the reaction zone in our experiments was probably somewhat above the value registered by the thermocouple at F (Fig. 1). Actually, the results fall within the range defined by Gomer and Noves⁶ at low temperatures and those of Bawn and Tipper at higher temperatures.* Furthermore, in the series II experiments in which the rate was so much faster than in I or III, the methane/ ethane ratio was distinctly higher, as might be expected if, due to lack of temperature equilibrium, the effective average temperature was higher than in the slower

¹¹ N. E. Berry and G. K. Rollefson, Phys. Rev. 38, 1599 (1931). * In the case of the latter authors, the pressures of carrier gas were so low that the recorded temperatures probably should be considered as minimum values. experiments. Considering all of these experiments, it seems justifiable to conclude that at low temperatures and over a wide range of pressures the dominant reaction for methyl radicals under these varied conditions is the formation of ethane. As the temperature is raised, the possibility of the methyl radical capturing a hydrogen atom from another radical, or some hydrogen containing molecule, increases corresponding to an activation energy for this reaction, which is about nine^{3, 6} kilocalories greater than that for the formation of ethane. The latter activation energy is usually assumed to be zero, but no conclusions concerning its value can be drawn from these experiments.

The variations in the yields of the substances found in smaller amounts in these experiments may be due, in part, to errors in analysis but may also be caused by slight variations in conditions which alter the relative importance of the various possible secondary reactions, although not affecting the principal association reaction of the radicals.

The results tabulated in Table II show that the products obtained as a result of the reaction of ethyl iodide with sodium in the vapor state consist of principally ethane, propane, and butane, with smaller amounts of ethylene, methane, and hydrogen. This is a greater variety than reported by Bawn and Tipper, who list only ethane, ethylene, and butane. There is no apparent reason for their failure to find the other products listed by us since, in this case, they give a material balance which is about the same as we have been able to get. It is noticeable in our results that although the absolute amounts of propane and butane show considerable variation, the sum of the two is reasonably constant. This fact suggests that the propane may not be a primary product but may result from the pyrolysis of butane. In order to check this idea, one of our fourth fractions, which analyzed as pure butane, was returned to the reaction vessel with the temperatures of the various parts set the same as for a regular run. After a short time the gas was pumped out, fractionated, and analyzed. It was found to contain about twenty-five percent propane. In view of this result, we believe that we are justified in considering the sum of the propane and butane as a measure of the amount of butane produced in the primary processes. On this basis it appears, from the results listed in Table II, that about twice as many moles of butane are produced as there are of ethane. Bawn and Tipper report that with ethyl iodide they obtained about two moles of ethane for each mole of butane over a range of temperature from 300 to 370°C with no apparent variation with temperature. This difference could still be explained as a temperature effect, as was done for the methyl iodide results above, if we consider that the trend is so much smaller in this case that it would be masked by experimental errors in the short range of temperatures covered by Bawn and Tipper. Saffer and Davis reported considerable quantities of ethane and propane with much smaller quantities of butane, butene, and propylene in their experiments with ethyl iodide. In view of our experience with the pyrolysis of butane, we are inclined to think that their reported values for three and four carbon hydrocarbons should be lumped together as a measure of the amount of butane formed originally. If this is done, their result agrees quite well with those of Bawn and Tipper for the same temperature. Our fastest runs (series VI), which presumably occurred at higher temperatures than the slower ones, seem to show some trend in the direction of higher ethane/butane ratios which would be in accord with the idea that the difference is due to difference in temperature in the reaction zone. However, the effect is too small to be considered certain.

Another point of difference between our results and those published previously is that we find considerably less ethylene. This fact can also be explained on a temperature dependence basis if we assume that the normal reaction of the ethyl radicals at low temperatures is to form butane, but at higher temperatures the disproportionation reaction and reaction with some other molecule to form ethane become important. For this explanation to hold it is necessary that the latter two possibilities require slightly higher activation energies than the formation of butane, which may not require any. This seems like a reasonable assumption.

At this point it seems desirable to review the work on the photolyses of mercury dimethyl and mercury diethyl. With regard to the former, both Cunningham and Taylor⁸ and Gomer and Noyes⁶ find that, at low temperatures, the dominant product is ethane with relatively little methane. As the temperature is increased, the methane/ethane ratio increases. The data of the latter authors may be plotted as log(methane/ ethane) vs 1/T to give a reasonably good straight line. In this manner their data may be extrapolated to the temperatures used by Bawn and Tipper, and it is found that they correspond to lower ratios than the latter give by about a factor of three. On the other hand, the extrapolated values are a little closer to the values obtained by Cunningham and Taylor in the thermal decomposition of mercury dimethyl at 348°C. They are also more in accord with our results. Although it has been postulated in this earlier work that the radicals might enter into reactions with the excess mercury dimethyl or a HgCH₃ radical, the results, when compared to those obtained from the reaction of sodium with methyl halides, seem to indicate that there is little, if any, specific effect of this nature.

A similar comparison can be made between the results obtained by Moore and Taylor⁹ for the photolysis of mercury diethyl and our results. Their butane/ethane ratio is a little lower than that found by us and decreases as the temperature is raised. The highest temperature they used was 250° C, at which their values were definitely below those obtained by Bawn and Tipper at 300° and higher. However, the discrepancy is not great, and it seems justifiable to conclude that the action of the radicals in this type of system is essentially the same as in the reactions of sodium with the ethyl iodide, whether the experiments are carried out at high or low pressures or in the presence of an inert carrier gas.

The variety of products reported in other systems in which methyl or ethyl radicals have been assumed as intermediates is probably due, to some extent at least, to specific interactions with the other molecules present, such as aldehydes or ketones. The system which does not seem capable of a simple explanation in terms of the results discussed in this paper is the photolysis of ethyl iodide in the presence of silver. West and Schlessinger reported finding only ethane and ethylene, although we would have expected a mixture of these substances with

a considerable amount of butane. Since this is the only case in which butane is not reported, it must be considered an exception, possibly due to the reaction occurring at the surface of the silver. In this connection, it may be mentioned that Bawn and Whitby¹² reported that the decomposition of silver ethyl in alcohol solution at -40° C yielded ethane and ethylene as well as some butane. If we were to extrapolate the other results discussed in this paper to such a temperature, we would not expect any appreciable amount of ethane and ethylene.

¹² C. E. H. Bawn and F. J. Whitby, Faraday Society Discussions 2, 228 (1947).

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The Bonding of Trihalide and Bifluoride Ions by the Molecular Orbital Method

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A simple molecular orbital treatment is presented to explain the bonding in trihalide ions, X₃-, XY₂-, and XYZ⁻, and bifluoride ion, HF₂⁻. The M.O.'s are formed from linear combinations of $np\sigma$ halogen orbitals, and the 1s hydrogen orbital and stable bonding M.O.'s are obtained without the introduction of higher atomic orbitals. Applications are suggested in prediction of other stable species and low energy reaction intermediates.

HE trihalide ions, X_3^- , XY_2^- , and XYZ^- , and bifluoride ion, HF2-, offer an interesting opportunity to test theories of molecular bonding. Both molecular halogen, X_2 , and the halide ion, X^- , have the appropriate number of electrons to provide completed octets. Hence, the formation of an additional covalent bond in X_3^- provides an excess of electrons over the number required to fill the outermost occupied porbitals. Consequently, a description of the electronic arrangement using only hydrogen atom orbitals must introduce at least one orbital of higher energy. Similarly, hydrofluoric acid, HF, and fluoride ion, F⁻, have electronic arrangements predicted to be particularly stable by the widely applicable Lewis covalent bond description. Bifluoride ion, with an additional bond, may be described in the conventional bonding scheme only if covalent bonds are abandoned (i.e., "ionic" bonding is assumed) or if an additional orbital contributes to the bonding. In HF_2^- the only available atomic orbitals are of higher principle quantum number and are presumably of much higher energy.

The electronic arrangements of I_3^- , ICl_2^- , IBr_2^- , and ClIBr⁻ have been discussed by Pauling,¹ and Kimball² has considered I₃⁻. Both authors utilize bond hybridization arguments to rationalize the use of a higher energy

¹L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940). ²G. E. Kimball, J. Chem. Phys. 8, 188 (1940).

5d or 6s orbital. Pauling¹ discusses the HF_2^- ion with an ionic bond description, averting the problems introduced by a covalent bond model.

X-ray studies of trihalide salts have been made for CsICl₂,³ and for N(CH₃)₄ICl₂, NH₄I₃, and NH₄ClIBr.⁴ Except for NH₄I₃, the trihalide group is found to be linear. The I_3^- group may deviate from linearity by a few degrees, and the central iodine atom seems to be nonequidistant from the end iodine atoms. The experimental halogen-halogen bond lengths, d, are slightly longer than predicted from the sums of the covalent radii, Σr , as given by Pauling.¹ The lowest ratio of $d/\Sigma r$ is found for N(CH₃)₄ICl₂ to be 1.01; and the largest ratio for the larger I-I distance in NH_4I_3 , is 1.16. The latter is much larger than the average ratio, 1.06. The trihalide bonds are apparently slightly longer and presumably slightly weaker than the corresponding halogen bonds.

Four bifluoride salts have been studied by x-ray analysis, KHF₂,⁵ NaHF₂,⁶ TlHF₂,⁷ and NH₄HF₂.⁸ The

- ³ R. W. G. Wyckoff, J. Am. Chem. Soc. 42, 1100 (1920). ⁴ R. C. L. Mooney, Z. Krist. (A) 100, 519 (1939); 90, 143 (1935); Phys. Rev. 47, 807 (1935).
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