[Contribution from the Department of Chemistry, Canisius College]

# Decomposition of the Liquid Alkyl Iodides by 120 kvp. X-Radiation[1]

By Robert H. Schuler[2a] and Robert C. Petry[2b]

Received March 12, 1956

The predominant products of the X-ray decomposition of liquid ethyl iodide, *n*-propyl iodide and isopropyl iodide are iodine and hydrocarbons of the same carbon number as the parent species. In general, unsaturated hydrocarbons are produced in a somewhat greater yield than saturated hydrocarbons and iodine is found in an amount in excess of that expected from the observed hydrocarbons. Minor yields of hydrogen, methane and other hydrocarbons are observed. Net products are formed by processes other than those involving thermal radicals since such radicals are removed by iodine necessarily present. Use of radioiodine in the scavenging reactions has shown that the radical yield results almost entirely from rupture of the carbon–iodine bond. A low yield of isomerization of *n*-propyl iodide, similar to the photolysis at 3261 Å. but in contrast to that at 2537 Å., indicates that a large fraction of the radicals are produced with little excess energy. Attention is called to other characteristic differences between the products of photolysis and radiolysis.

Iodine production in the radiation decomposition of the alkyl iodides has been studied by a number of investigators who have used as the source of activation the mixed radiation from a 300 millicurie radium–beryllium neutron source,[3] radon alpha particles,[4] 1–4 Å. X-rays,[4] 50 kvp. X-rays,[5] fast electrons[6] and Mev. X-radiation.[6] Except for earlier work on the radiolysis of methyl iodide,[7] no attention has been given to the gaseous products of the decomposition. This contribution reports extension of the gas production studies to the higher iodides along with further work on the formation of iodine and free radicals.

## Experimental

**Alkyl Iodides.**—Commercial alkyl iodides were washed with thiosulfate solution and water, dried and passed through a silica gel column. The center cut from a simple distillation was fractionated through a three-foot helix-packed all-glass column. In the case of the propyl iodides this fractionation was carried out at reduced pressure in order to avoid the decomposition which occurs at the normal boiling point. The silica gel treatment caused some decomposition, particularly in the case of isopropyl iodide where considerable iodine was liberated. Any iodine formed was removed in the following distillations. Center cuts from the fractional distillation, which had constant boiling points and indexes of refraction, were used in the irradiations. These samples showed little decomposition when stored in the dark.

**Irradiation.**—The irradiations were carried out as previously described[7] using as the radiation source an X-ray unit operated at 5 ma. and 120 kvp. All samples were of 10-ml. volume and were contained in a 50-ml. florence flask which could be attached to a high-vaccum line through a stopcock and ground joint. They were irradiated in the position of maximum X-ray dosage with the radiation entering vertically through the bottom of the flask. Prior to introduction into the irradiation cell, the samples were distilled through a simple still to remove the bulk of the dissolved gas. The samples were then repeatedly frozen in liquid nitrogen, pumped and melted and finally degassed at −115°.

**Gas Measurement and Analysis.**—The general methods of gas measurement and analysis have been previously described.[7,8] The hydrogen–methane fraction was taken as that volatile at liquid nitrogen temperature. In the case of ethyl iodide, the hydrocarbon products were separated by freezing the sample at the temperature of ethyl bromide–butyl bromide mush (∼ −125°) and trapping the volatile material at liquid nitrogen temperature. The sample was then closed off from the pumping system, the temperature of the trap was raised to −125° and the $C_2$ fraction pumped to the measuring McLeod gage. The $C_3$ fraction from the propyl iodides was separated at −50 to −60°, trapped at liquid nitrogen temperature and finally pumped from the trap at −115°. A total of 15 to 20 degassing operations was required for each sample. All gas measurements were followed by combustion on copper oxide and in the case of the $C_2$-$C_3$ fractions by hydrogenation.

Removal of the $C_3$ hydrocarbons from the samples was checked in the following manner. A sample of 34.5 μmoles of propane was distilled onto 10 cc. of degassed propyl iodide. A total of 36.0 μmoles of gas was recovered in 15 degassing operations. In this case the individual fractions were separately measured. In normal degassings, the samples were accumulated and a smaller error is involved in the total. The gas yields are believed accurate to about 5%.

A portion of the $C_2$-$C_3$ sample from the 200 min. irradiations of each of the iodides was sealed in a tube and submitted for mass-spectrometric analysis.[9] The remaining portion of the $C_2$-$C_3$ fraction was retained for analysis by combustion and hydrogenation. The total $C_2$-$C_3$ sample from the propyl iodides, after measurement, was subjected to a final fractionation from a tube attached to the gas analysis apparatus and maintained at −115°. Respectively, 96 and 97% of the sample was recovered and the condensable material was rejected from the analysis.

**Iodine Production.**—The production of free iodine was followed spectrophotometrically during the course of the irradiation of a single sample by determining the optical density in a Pyrex absorption cell attached to the irradiation vessel. Measurements were made at 460, 500 and 520 mμ. Coloration of the cuvette during the irradiation was avoided by placing it in a position in which it was shielded from the X-ray beam. The samples from the longer irradiations made for gas production studies were determined spectrophotometrically after appropriate dilution.

**Free Radical Identification.**—The experiments of Gevantman and Williams[10] on the detection and identification of the radical fragments formed in the radiolysis of the alkyl iodides have been repeated using a modified wash-out isolation of the carrier materials. Radioiodine[11] was added, the sample was degassed and irradiated, the iodine produced was extracted from the sample and equal volumes of carrier iodides were added. The carriers were then separated as previously described.[12] In the case of the propyl iodides, 100 mg. of iodine was added to the carrier mixture and extracted the following day. The small fraction of activity which exchanged with the molecular iodine is tentatively ascribed to the formation of an unsaturated iodide such as allyl iodide. Products such as this can cause great difficulty

---

[1] This work was supported in part under Contract AT (30-1-)-1084 with the U. S. Atomic Energy Commission. Presented at the 124th Meeting of the American Chemical Society in Chicago, Ill., September 11, 1953.

[2] (a) Brookhaven National Laboratory, Upton, N. Y.; (b) Ohio State University, Columbus, Ohio.

[3] P. Sue and E. Saeland, *Bull. soc. chim. France*, 437 (1949).

[4] M. Lefort, P. Boney-Maury and M. Frilley, *Compt. rend.*, **226**, 1904 (1948).

[5] E. L. Cochran, W. H. Hamill and R. R. Williams, Jr., This Journal, **76**, 2145 (1954).

[6] R. H. Schuler and W. H. Hamill, *ibid.*, **74**, 6171 (1952).

[7] R. C. Petry and R. H. Schuler, *ibid.*, **75**, 3796 (1953).

[8] R. H. Schuler and C. T. Chmiel, *ibid.*, **75**, 3792 (1953).

[9] Analyzed by Consolidated Engineering Corp., Pasadena, California.

[10] L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

[11] $I^{131}$ obtained through the U. S. Atomic Energy Commission, Oak Ridge, Tenn.

[12] R. G. Badger, C. T. Chmiel and R. H. Schuler, This Journal, **75**, 2498 (1953).

in the radical identifications if they contain radioiodine with a high specific activity, since they readily exchange with the carrier materials during the distillations.[12]

## Results

The linear production of iodine with dose is illustrated in Fig. 1. In the case of methyl and ethyl iodide, the decomposition was followed for a total irradiation period of 100 min. and found to have the same constant yield shown in the figure. The iodine production rates taken from the slopes of these curves are given in Table I. The iodine production rates observed in the gas production studies are slightly lower. This decrease is possibly due to contamination of the sample with mercury during the lengthy degassing procedure employed in the determination of volatile products. The ratio of yields from ethyl, *n*-propyl and isopropyl iodide, 1:0.71:1.29, may be compared with the ratio, 1:0.86:1.26, reported by Cochran, Hamill and Williams.[5]

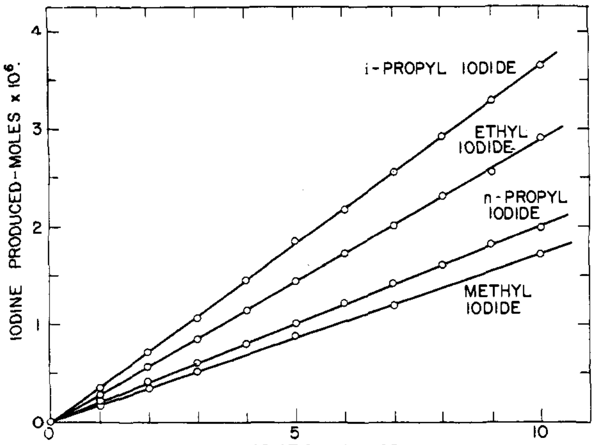

Fig. 1.—Iodine production.

TABLE I

RELATIVE X-RAY DECOMPOSITION YIELDS

| Iodide | Irradiation period,[a] min. | Product formation rate, moles/min. × 10⁸ $I_2$ | $H_2$ | $CH_4$ | $C_2$–$C_3$[b] | $C_2$–$C_3$ fraction *n*C | Unsaturation[c] |
|---|---|---|---|---|---|---|---|
| Methyl | [d] | 16.5 | 1.1 | 7.8 | 16.3 | .. | 0.100 |
| Ethyl | 10 | 28.5 | 2.8 | .. | 48.5 | 1.96 | .619 |
| | 50 | 23.1 | 2.8 | 0.1 | 44.5 | 2.00 | .631 |
| | 100 | 22.0 | 2.9 | .1 | 44.3 | 1.97 | .650 |
| | 200 | 22.6 | 2.8 | .1 | 45.1 | 2.02 | .676 |
| | | | | | | (1.99)[e] | ( .673)[e] |
| | 0– 25 | 27.8[f] | | | | | |
| | 0–100 | 28.2[f] | | | | | |
| *n*-Propyl | 100 | 19.0 | 3.5 | 0.2 | 38.9 | 2.84 | .597 |
| | 200 | 18.0 | 3.6 | .2 | 34.7 | 2.86 | .582 |
| | | | | | | (2.89)[e] | ( .585)[e] |
| | 0 –10 | 19.8[f] | | | | | |
| Isopropyl | 100 | 32.0 | 3.6 | .1 | 69.7 | 2.96 | .568 |
| | 200 | 30.5 | 3.4 | .2 | 57.5 | 2.94 | .553 |
| | | | | | | (2.99)[e] | ( .538)[e] |
| | 0 –10 | 36.4[f] | | | | | |

[a] Energy is absorbed in the iodides at the rate of 8.3 × $10^{17}$ e.v./min. [b] Fraction volatile at −115° or −125°; *cf.* Table II for analytical data. [c] Double bonds per molecule. [d] *Cf.* reference 7. [e] Calculated from mass spectrometric data. [f] Relative yield of iodine observed during intermittent irradiation of sample.

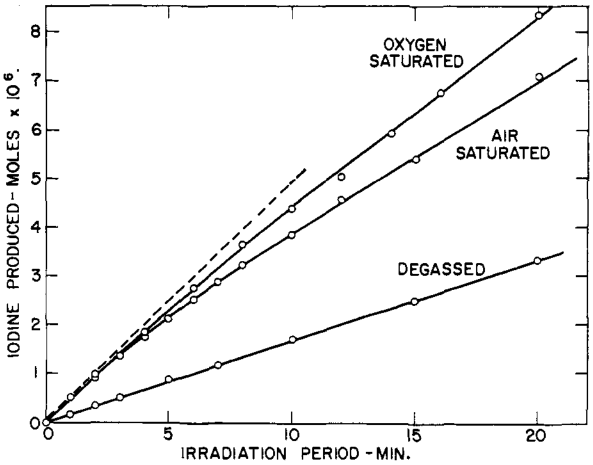

Fig. 2.—Effect of dissolved oxygen on iodine production from methyl iodide.

Figure 2 illustrates the production of iodine in air-saturated and oxygen-saturated methyl iodide. In these solutions the rate of iodine production decreases as the iodine builds up in the sample due to competition between the iodine and dissolved oxygen for the radicals produced by the radiation. It is estimated that the initial rate of iodine production from air-saturated methyl iodide is 50 × $10^{-8}$ mole/min. Similar data for air-saturated ethyl iodide give an initial rate of 56 × $10^{-8}$ mole/min.

The observed rates of gas production are given in Table I which also includes a summary of the results from the previous work on methyl iodide.[7] The last two columns in the table give the carbon number and degree of unsaturation of the $C_2$–$C_3$ fractions. The mass spectrometric analytical data for the $C_2$–$C_3$ fractions from the 200 min. irradiations are given in Table II.

TABLE II

MASS SPECTROMETRIC ANALYSIS OF $C_2$–$C_3$ FRACTIONS

| | Methyl iodide | Ethyl iodide | *n*-Propyl iodide | Isopropyl iodide |
|---|---|---|---|---|
| Sample; moles × $10^6$ | 42 | 60 | 36 | 50 |
| Product, mole % | | | | |
| Ethane | 88.6 | 34.2 | 0.2 | 0.1 |
| Ethylene | 6.8 | 60.7 | 5.2 | 0.1 |
| Acetylene | 2.6 | 3.3 | 1.6 | .. |
| Propane | 0.4 | 0.2 | 40.7 | 45.3 |
| Propylene | 0.1 | .. | 50.1 | 53.6 |
| $C_4$ | 0.04 | 0.1 | .. | .. |
| $CO_2$ | 1.4 | 1.6 | 2.2 | 0.3 |

For ethyl iodide the hydrogen and $C_2$ yields are independent of the radiation dose with little, if any, induction effect observed. The yield of methane is low and difficult to determine accurately because of the large excess of hydrogen. It is estimated that about 3% of the liquid nitrogen volatile fraction is methane. The slight trend in the unsaturation values of the $C_2$–$C_3$ fractions is not believed to be of significance. The unsaturation as determined by hydrogenation is in excellent agreement with the mass spectrometric value determined on another portion of the same sample. The carbon numbers show the material volatile at −125° to be predominantly $C_2$ hydrocarbons in all cases.

For the propyl iodides the yield of hydrocarbon products appears to drop slightly as the irradiation progresses. The carbon numbers and unsaturation

TABLE III

RADICAL IDENTIFICATION

| Iodide | Radioiodine added, moles/l. | Irrad. period, min. | Exchange, % | Total organic activity, c./min. | % activity as[a] $CH_3I$ | $C_2H_5I$ | $i$-$C_3H_7I$ | $n$-$C_3H_7I$ | $CH_2I_2$ | Exch.[c] | Material[b] balance |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl | 0.0029 | 100 | 73.8 | 2739 | 96.5 | 0.7 | .. | .. | 2.8 | .. | 1.002 |
| Ethyl | .0054 | 100 | 44.2 | 2170 | 1.0 | 95.8 | 2.3 | 0.2 | 0.7[d] | .. | 1.025 |
| | .0004 | 50 | 75.8 | 9303 | 1.0 | 96.5 | 1.0 | 0.5 | 1.0[d] | .. | 0.990 |
| $n$-Propyl | .0022 | 45 | 39.7 | 6820 | 1.6 | 0.2 | 4.3 | 86.3 | 2.7 | 4.9 | 0.970 |
| Isopropyl | .0010 | 50 | 48.3 | 6890 | 1.0 | 0.4 | 94.0 | 1.2 | 1.0[d] | 2.4 | 0.985 |

[a] Calculated as the ratio of the individual activity to the sum of the activities of the measured components. [b] The ratio of the sum of the activities of the individual components to the activity of the total sample. [c] Activity exchanging with $I_2$ overnight at room temperature. [d] No excess activity was found in the pot residue.

values show little effect of extent of irradiation on the composition of the gas. From each of the propyl iodides hydrogen is produced in an amount proportional to the dose and a yield of methane about 5% that of hydrogen is observed.

The results of the radical identification experiments in Table III show considerably lower yields of minor products than reported by Gevantman and Williams.[10] It is believed that the separation procedures employed here provide results which are significant to 0.1–0.2% in the methyl iodide fraction and to about 0.5% in the higher boiling components.[12] The formation of small amounts of methyl iodide from each of the higher iodides appears to be unquestionably real as does the formation of isopropyl iodide from $n$-propyl iodide. The activities observed in the other components are marginal since the appearance of iodine exchangeable activity introduces complications as mentioned above. Indeed, the yields of products other than the parent material are surprisingly low. The lack of a high degree of isomerization of $n$-propyl iodide is of particular interest since this isomerization occurs to a much smaller extent (4.3%) than might be expected from the high yield (28%) observed by McCauley, Williams and Hamill[13] in the photolysis at 2537 Å. Isomerization of isopropyl iodide (1.2%) is also lower than that in photolysis (4%). The present work emphasizes even more strongly the generalization of Gevantman and Williams,[10] that the majority of bond ruptures in the radiolysis of the alkyl iodides occurs in the carbon–iodine bonds.

**Radiation Yields.**—Recalibration of the $Co^{60}$ source used in the previous work[7] with a ferrous sulfate solution containing millimolar sodium chloride has shown the given rate of oxidation to be too high. Correcting the present measurements for source decay, the rate of ferrous oxidation is $0.193 \times 10^{-8}$ equil./10 ml./min. Assuming that the absorption of the $Co^{60}$ $\gamma$-radiation per unit volume of sample is 2.03 times greater for the methyl iodide than for water,[7] the yield of iodine ($G(I_2)$) from methyl iodide is calculated as 1.20.[14] This yield is based on a value of 15.5 for the Fricke (ferrous sulfate) dosimeter. Due to the high relative absorption of weak scattered radiation by the methyl iodide,[15] this yield is probably very slightly high. The present work has confirmed the previously given rate of oxidation of ferrous ion in the X-ray source ($18.0 \times 10^{-8}$ equil./min.).

The presence of iodine makes the photoelectric absorption coefficient of the samples very high in the X-ray experiments so that essentially all (96% in the case of methyl iodide) of the incident energy is absorbed in the material. Because of this the absorbed energy is independent of the sample size, and the relative yields are expressed as total product rather than in terms of concentration as is common in higher energy sources. The relative yields for the different materials are directly measured by the observed production rates. Although the concentration of iodine in the propyl iodides is only two-thirds of that in methyl iodide, the difference in energy absorption is negligibly small (94% as compared to 96%).

The absolute yields for the various products are given in Table IV based on the rate of $1.65 \times 10^{-8}$ moles/min. equivalent to a radiation yield of 1.20. For the gaseous products, the yields are calculated from the 200 min. irradiations where mass spectrometric analytical data are available. The iodine yields are calculated from the results shown in Fig. 1. The methyl radical yields are given from the data of the iodine scavenging experiments with the assumption that the total exchange yield is $8 - G(I_2)$.[16] The relatively high over-all yield of exchange magnifies the importance of the minor components of Table III with respect to the other components.

TABLE IV

RADIATION YIELDS, MOLECULES PER 100 EV.

| | Methyl iodide | Ethyl iodide | $n$-Propyl iodide | Isopropy iodide |
|---|---|---|---|---|
| $H_2$ | 0.08 | 0.20 | 0.26 | 0.25 |
| $CH_4$ | .57 | .007 | .015 | 0.015 |
| $C_2H_6$ | 1.05 | 1.12 | .005 | 0.004 |
| $C_2H_4$ | 0.08 | 2.00 | .13 | 0.004 |
| $C_2H_2$ | .03 | 0.11 | .04 | 0.00 |
| $C_3H_8$ | .005 | .007 | 1.03 | 1.89 |
| $C_3H_6$ | .001 | .00 | 1.27 | 2.25 |
| $I_2$ | 1.20 | 2.03 | 1.44 | 2.65 |
| $CH_3\cdot$ | .. | 0.06 | 0.10 | 0.05 |
| Isomer | .. | .. | .28 | 0.06 |

## Discussion

The amounts of products formed in the radiolysis of the alkyl iodides are to a very good first approximation directly proportional to the radiation dose

---

(13) C. E. McCauley, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **76**, 6263 (1954).

(14) All radiation yields ($G$ values) are expressed here as molecules produced per 100 e.v. of energy absorbed by the system.

(15) W. Bernstein and R. H. Schuler, *Nucleonics*, **13**, No. 11, 110 (1955).

(16) R. H. Schuler, D. H. McKenney and W. H. Hamill, to be published.

received by the sample. However, for extended irradiations, where the iodine builds up to about $0.5 \times 10^{-3}$ mole fraction, a slight decrease in the yield is observed. In the case of methyl iodide it has been shown[7] that the presence of dissolved iodine at this concentration results in only a several per cent. decrease in the yield of gaseous products, although a considerably greater effect occurs at higher concentrations. Since the photolysis of the higher iodides appears to be more complex than that of methyl iodide,[13] the corresponding radiolysis is also expected to be more complicated and conceivably could be affected to a greater extent by the presence of iodine.

The lack of an appreciable induction period is due to the fact that, as in the photolysis,[17] the first trace of free iodine produced by the initial irradiation is sufficient to quench all homogeneously distributed thermal radicals. Reaction 1, which oc-

$$R\cdot + I_2 \longrightarrow RI + I\cdot \qquad (1)$$

curs in the presence of even small amounts of iodine, prevents the radical concentration from rising to the point where radical combination reactions can effectively compete. Reaction 2 does not, there-

$$R\cdot + R'\cdot \longrightarrow RR' \qquad (2)$$

fore, occur as a homogeneous reaction in the bulk of the solution. Whether or not it is important as a track process awaits further experimentation.

The absorption of an iodine atom by Reaction 1 removes the iodine atom produced in the original decomposition so that there is no net product formation. Observable products are formed only by reactions other than those involving homogeneously distributed thermal radicals, *i.e.*, by hot radical reactions, by reactions of highly excited and ionic species and by processes occurring at the high radical concentrations present in the track of the ionizing particle.

Underlying the stoichiometry of the decomposition of ethyl iodide is reaction 3 to which the equiva-

$$2C_2H_5I \longrightarrow C_2H_6 + C_2H_4 + I_2 \qquad (3)$$

lent of reaction 4 must be added to account for

$$2C_2H_5I \longrightarrow 2C_2H_4 + H_2 + I_2 \qquad (4)$$

hydrogen production. The observed material balance is, however, not particularly good. The hydrogen produced amounts to only about two-fifths of the excess unsaturation. Some hydrogen iodide, which was not quantitatively determined in this work, is formed and detected by fuming of the sample upon exposure to air.

In the case of *n*-propyl iodide the material balance is somewhat better in that the hydrogen yield is equivalent to the excess of propylene over propane. Additional unsaturation is attributable to the formation of ethylene by the cracking of the propyl radical according to reaction 5. For iso-

$$CH_3CH_2CH_2\cdot \longrightarrow CH_3\cdot + C_2H_4 \qquad (5)$$

propyl iodide the hydrogen observed accounts for about 65% of the excess propylene over propane.

In contrast to the low yields of hydrogen, in general, iodine is produced in an amount greater than can be accounted for by the observed hydrocarbon products. The high iodine yields suggest that higher hydrocarbons are formed by reactions similar to those which produce ethane in the radiolysis of methyl iodide,[7] *e.g.*, for ethyl iodide

$$2C_2H_5I \longrightarrow C_4H_{10} + I_2 \qquad (6)$$

Very little fragmentation of the carbon skeleton occurs as can be seen from the low yields of methyl radicals and from the almost complete lack of ethyl radicals from *n*-propyl iodide. Methyl and methylene iodides presumably can be formed from ethyl iodide by rupture of the carbon–carbon bond followed by quenching of the free radicals by the iodine present. The methyl and methylene iodide

$$C_2H_5I \longrightarrow CH_3\cdot + CH_2I\cdot \qquad (7)$$

are observed in equivalent amounts. In the case of *n*-propyl iodide, reaction 5 accounts for a large fraction of the observed methyl iodide leaving few methyl radicals to be formed by the rupture of the terminal carbon–carbon bond. In the case of isopropyl iodide no fragmentation path analogous to 5 is available to the isopropyl radical, so that the observed yield presumably is a measure of terminal bond rupture. Since two methyl groups are present in isopropyl iodide, it is seen that methyl radical production per methyl group present is only about one-fourth that from *n*-propyl iodide. Lack of activity in the pot residue in excess of that due to the methylene iodide implies that the production of stable diiodides, such as 1,1-diiodoethane, is negligible and that the $\alpha$-hydrogen atoms are not susceptible to attack by the radiation.

In studies of iodine production from the alkyl iodides, Cochran, Williams and Hamill[5] have called attention to the fact that similar relative yields of iodine are found in radiolysis and photolysis. We have previously pointed out[6,7] that methyl iodide is an exception to this rule of similarity since the iodine yield is very low in the photolysis ($\phi_{2537}(I_2) = 0.008$) but is quite appreciable in the radiolysis ($G(I_2) = 1.2$). The similarity of the iodine yields from the higher iodides would be anticipated since primary dissociation processes analogous to those operative in the photolysis must certainly be present in the radiation decompositions. Since the quantum yield for $I_2$ production is high ($\phi(I_2) \sim 0.2$) for the alkyl iodides other than methyl, other components of $I_2$ production will become obscured. In methyl iodide, however, since the quantum yield for iodine production in the photolysis is very low, the particular features of the radiolysis become more pronounced.

In the examination of the gaseous products, minor constituents are emphasized, and other non-similarities between the photolysis and radiolysis become evident. McCauley, Williams and Hamill,[13] in studies of the photolysis of the propyl iodides, have shown that very nearly equivalent amounts of saturated and unsaturated hydrocarbons are formed. Although the mechanism of the photolytic decomposition of the pure iodides appears to be more complex than originally anticipated,[13] the stoichiometry can be represented by 8.

$$2C_nH_{2n+1}I \longrightarrow C_nH_{2n+2} + C_nH_{2n} + I_2 \qquad (8)$$

The present results show that in the radiolysis the

---

[17] W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951).

unsaturated hydrocarbon is produced in a yield in excess of the saturate. Hydrogen and small amounts of other products are also formed. It is evident that, while a large fraction of the decomposition does proceed in a manner analogous to that of the photolysis, there are other reactions of varying importance that do contribute. One must be careful not to overgeneralize the similarities that do exist.

The predominant effect of the radiolysis of the alkyl iodides is the rupture of the C–I bond. This occurs in spite of the fact that an appreciable fraction of the energy is initially absorbed by the hydrocarbon part of the molecule. It appears, therefore, that absorbed energy is rapidly distributed over the whole molecule and results in primary chemical dissociations which are characteristic of the activated species. In the present case preferential rupture is expected to occur upon localization of energy in the weaker carbon–iodine bond. Exclusive rupture of this bond in the alkyl iodides is of course known for low energy quanta from spectroscopic[18] and photochemical[8] considerations. In a similar manner organic acids are known to undergo preferential decarboxylation.[19] McDonell and Newton[20] have found that in the high energy irradiation of the aliphatic alcohols the energy is directed to the α carbon atom.

There is one other very important aspect to the present work. McCauley, Williams and Hamill have reported that in the photolysis of *n*-propyl iodide at 3261 Å. there is very little isomerization (~ 3%) of the *n*-propyl radical. Under more energetic conditions at 2537 Å. there is observed an appreciable yield of isomer (~ 28%). In the present work isomerization amounts to only about 4%. This very strongly indicates that a large majority of the radicals result from processes in which barely sufficient energy is given to the molecule to rupture the C–I bond. This contrasts with the assumption frequently made that since ionizing radiation is very energetic, a very drastic effect upon the system is produced. As is of course evidenced by the formation of minor products, some reactions do occur which involve a considerable amount of energy. In a large majority of the cases, however, the processes represent a minimum of energy in the reacting system.

BUFFALO 8, NEW YORK

[18] G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

[19] I. A. Breger, *J. Phys. Colloid Chem.*, **52**, 551 (1948).

[20] W. R. McDonell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Acetato Complexes of Lead in Aqueous Solution

BY EUGENE A. BURNS[1] AND DAVID N. HUME

RECEIVED FEBRUARY 17, 1956

The existence of three complex ions, $Pb(OAc)^+$, $Pb(OAc)_2$ and $Pb(OAc)_3^-$ has been shown in perchlorate solutions of lead containing excess sodium acetate and acetic acid. By the use of polarographic, potentiometric and solubility techniques successive "over-all" formation constants have been evaluated at an ionic strength of 1.98 *M*. The average values of the "over-all" formation constants obtained by the three techniques for the mono-, di- and tri-acetato complexes are 145, 810 and 2950, respectively. The presence of anionic species was confirmed by means of an anion-exchange technique.

The formation of complex ions by lead salts in acetate media has been investigated in the past by several authors.[2–8] The striking disagreement among them both as to the number and stability of the complexes formed is illustrated by the results summarized in Table I. In almost every instance there has been some evident source of potential error: the use of nitrate media, which have recently been shown to cause complex formation with lead,[9,10] variable ionic strength or standard state, insufficient range of acetate concentrations to show the existence of higher complexes or *p*H so high as to introduce the possibility of forming hydroxo-lead-(II) ions. This unsatisfactory state of affairs prompted the present study in which we have investigated the reactions between lead and acetate ions in a buffered perchloric acid medium of constant ionic strength by three independent methods: potentiometric, polarographic and solubility.

## Experimental

**Polarography.**—Measurements were made with a Sargent Recording Polarograph Model XXI. Corning marine barometer tubing was used for the capillary, which had a value of 1.36 mg.$^{2/3}$ sec.$^{-1/2}$ for $m^{2/3}t^{1/6}$ in 2.0 *M* sodium perchlorate at the potential of the saturated calomel electrode. The temperature was maintained at 25.0 ± 0.3°. No maximum suppressor was found to be necessary.

In order to obviate irreproducible results, which are found due to precipitation of potassium perchlorate at the interface when the conventional saturated calomel electrode is used in conjunction with a perchlorate medium, a calomel electrode saturated in sodium chloride rather than potassium chloride was utilized. The potential of the reference electrode was found to be within 1 mv. of the conventional electrode at 25°. The saturated calomel electrode was connected by means of saturated sodium chloride—3% agar-agar salt bridge to a reservoir of 1.98 *M* sodium perchlorate

---

[1] Abstracted from a thesis submitted by Eugene A. Burns in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the Massachusetts Institute of Technology, 1956.

[2] A. Jacques, *Trans. Faraday Soc.*, **5**, 225 (1909).

[3] S. M. Edmonds and N. Birnbaum, THIS JOURNAL, **62**, 2367 (1940).

[4] B. C. Purkayashta and R. N. Sen-Sarma, *J. Ind. Chem. Soc.*, **23**, 31 (1946).

[5] N. K. Das, S. Aditya and B. Prasad, *ibid.*, **29**, 169 (1952).

[6] S. Aditya and B. Prasad, *ibid.*, **30**, 213 (1953).

[7] V. F. Toropova and F. M. Batyrshina, *Zhur. Anal. Khim.*, **4**, 337 (1949).

[8] S. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Section*, **74**, 531 (1953).

[9] H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953).

[10] A. I. Briggs, H. N. Parton and R. A. Robinson, *ibid.*, **77**, 5840 (1955).