[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, ST. PETER'S COLLEGE AND BROOKHAVEN NATIONAL LABORATORY]

Radical Production in the Radiolysis of Liquid Butane[1]

BY CHARLES E. MCCAULEY AND ROBERT H. SCHULER[2]

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The distribution of radical species produced during the radiolysis of liquid butane has been studied by the radioiodine scavenging method. While the radiation yield for formation of total alkyl iodide product increases from a value of 5.6 molecules per 100 electron volts at an iodine concentration of 2×10^{-3} *M* to a value of 9 at 2×10^{-2} *M*, the yield for each of the monoiodide products is constant. These yields are, respectively, 0.4, 0.9, 0.1, 0.0, 1.0 and 2.1 for methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and *sec*-butyl iodides. The increase in yield of total organic iodides at the greater iodine concentrations is due to a large increase in the yield of higher boiling material which most probably represents diiodide products. The constancy of the yields for the less complex products appears to be an additional indication of the validity of the iodine scavenging method since hydrogen abstraction reactions of the radicals are not affected by changes in the scavenger concentration in the region studied.

Radical production in the radiolysis of liquid hydrocarbons has previously been studied by employing iodine at low concentrations to scavenge the radicals formed.[3-6] It has been shown that the radiation yield for uptake of iodine is independent of concentration below 5×10^{-3} *M* and is presumably a good measure of the yield of radicals produced. The present investigation was undertaken in order to obtain information on the fragmentation pattern in the radiation decomposition of a typical liquid aliphatic hydrocarbon. Liquid butane was chosen since previous experience had shown it possible to obtain adequate separation of the expected alkyl iodides with boiling points up to that of *n*-butyl iodide[7,8] while at the same time the butane molecule is complex enough to allow for the possibility of several different modes in the resulting decomposition. In this work, radioiodine has been used as the detector and the yields of individual products have been determined by carrier isolation methods similar to those originally employed by Gevantman and Williams in studies of the radical distribution in the radiolysis of hydrocarbon vapors.[9]

Experimental

Materials.—Matheson C.P. *n*-butane, stated to be 99.0% pure, was used without further purification. Partition chromatograms of this material showed two barely detectable impurities below the butane peak and none above it, the indicated impurity being of the order of several tenths of a per cent. The alkyl iodides used as carriers were purified by washing with aqueous thiosulfate, drying over anhydrous magnesium sulfate and distilling at reduced pressures through a six foot packed column.

Sample Preparation and Irradiation.—A weighed quantity of radioiodine (5–45 mg.) was placed in the irradiation cell which was then cooled in liquid nitrogen and evacuated. Butane was condensed into a reservoir on the vacuum line and the desired quantity (7–9 cc.) distilled into the irradiation cell. The sample was frozen in liquid nitrogen, evacuated and sealed and the exact weight determined upon opening the cell after irradiation. The irradiation cells consisted of 8.5 mm. i.d. heavy-walled tubing 150 mm. long. Irradiations were carried out at 25° inside a cylindrical Co^{60} source of 30,000 roentgens per hour intensity.[10]

Product Analysis.—The extent of reaction of iodine was determined, as in previous work,[6] by measuring the fraction of iodine found to be organically combined after thiosulfate extraction. The radiation yield was calculated from this information combined with knowledge of the initial iodine concentration and energy absorbed by the sample. Together with the ratios of the activity of the individual components to that of the total sample this served to give the yields for each of the products.

After irradiation, the sample was cooled to about −40°. opened and added to a total of about 250 cc. of precooled mixed carriers. In general, transfer of the sample to the carriers appeared to proceed with little difficulty. The carrier mixture was allowed to come to room temperature and a portion taken for measurement of the ratio of *organic* activity to *total* activity. The bulk of the mixed carriers was then extracted with thiosulfate solution and a portion of this extracted mixture reserved for measurement of the specific activity. The remainder was separated into the individual components by fractional distillation at reduced pressure in a manner similar to that employed in earlier work.[7,8] The relative activities of the various fractions were measured in an annular jacketed geiger counter after a tenfold dilution with carbon tetrachloride. Because of this dilution, differences in the density of the various solutions were slight and resulted in correspondingly small variations in the counting efficiency. Appropriate corrections were, however, applied where necessary. The total activity of a particular component was determined from its specific activity and the volume of carrier initially added. The carriers consisted of 25–50 ml. of each of the suspected components together with about 5 g. of inactive iodine which was added to the mixture for the purpose of diluting any possible reaction between the active iodine present and the carriers. Of the butyl iodides, only *n*-butyl and *sec*-butyl iodide were added as carriers. Since the formation of isobutyl and *t*-butyl iodide involve somewhat complicated rearrangements, these iodides are not expected in any appreciable yield. However, any isobutyl iodide formed would have been carried in the *sec*-butyl iodide fraction while *t*-butyl iodide would have exchanged with the large amount of inactive iodine added[7] and hence would not appear as organic activity. In addition to the activity found in the added carriers, it was observed that the residue remaining in the stillpot after take off of a representative methylene iodide fraction had a higher specific activity than the methylene iodide itself. The activity in excess of the methylene iodide component is here referred to as the residue and presumably consists largely of high boiling diiodides. The total activity in this fraction was determined from the volume of material remaining in the stillpot and the specific activity of this residue.

Results

Radiation Yield for Uptake of Iodine.—Results of the radiochemical measurement of the fractional

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[2] Department of Radiation Research, Mellon Institute, Pittsburgh, Pennsylvania.

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TABLE I

DISTRIBUTION OF ALKYL IODIDES PRODUCED IN THE RADIOLYSIS OF IODINE SOLUTIONS IN LIQUID BUTANE

Iodine concn., *M*	Irradiation period, min.[a]	Reaction, %	Specific rate,[b] moles/g./min. × 10^9	Product distribution, %[c]								Material balance[d]
				CH_3I	C_2H_5I	*i*-C_3H_7I	*n*-C_3H_7I	*s*-C_4H_9I	*n*-C_4H_9I	CH_2I_2	Residue	
0.0024	702	25.84	1.56	8.2	16.4	0.7	1.6	37.5	18.2	11.2	6.2	1.052
.0046	780	14.85	1.53	11.0	16.5	0.3	1.9	34.5	18.0	11.3	6.5	0.990
.0093	1500	16.9	1.85	6.4	..	..	..	..	..	..	..	...
.0113	1157	11.57	1.94	20.5	14.5	0.3	2.0	29.5	16.0	9.9	7.3	0.971
.0189	2340	17.0	2.42	7.4	..	..	..	..	..	..	..	...
.0214	3460	20.76	2.23	4.4	11.2	0.3	1.3	29.0	12.6	17.2	24.0	1.002
.0230	1578	9.56	2.47	10.1	9.3	0.5	1.3	23.0	10.8	16.4	28.6	1.006

[a] Corrected for decay of source; dose rate in butane is 3.30 × 10^{16} e.v./g./min. [b] Ferrous oxidation rate in Fricke dosimeter is 8.25 μM/min. [c] Per cent. of the sum of the individual activities. [d] Ratio of the sum of the individual activities to that of the total sample.

TABLE II

RADIATION YIELDS[a]

Iodine concn., *M*	Total organic iodide	CH_3I	C_2H_5I	*i*-C_3H_7I	*n*-C_3H_7I	*s*-C_4H_9I	*n*-C_4H_9I	CH_2I_2	Residue
0.0024	5.71	0.47	0.94	0.04	0.09	2.14	1.04	0.64	0.35
.0046	5.59	.62	.92	.02	.10	1.93	1.01	.63	.36
.0093	6.7	.43	..	..	..	..	..	..	..
.0112	7.09	1.44	1.02	.02	.14	2.07	1.12	0.69	0.52
.0189	8.9	0.65	..	..	..	..	..	..	..
.0214	8.15	.36	0.91	.03	.11	2.36	0.99	1.40	1.96
.0230	9.05	.91	.84	.05	.12	2.08	.98	1.48	2.56

[a] Molecules of product per 100 e.v. of absorbed energy.

reaction of iodine are given in Table I along with the corresponding specific rates observed in each of the experiments. These rates are expressed in units of moles of total alkyl iodide product per gram of sample per minute of exposure in the 30,000 roentgens/hr. source. Absolute radiation yields were determined by comparison with the specific rate of ferrous iron oxidation in the Fricke dosimeter. Correction has been made for decay of the Co^{60} source to November 1, 1955, at which time the rate of ferric ion formation was 8.25 μM/min. The corrected irradiation periods are given in Table I. Assuming that $G(Fe^{+++})$ is 15.5 and that energy absorption is proportional to the electron density of the irradiated material, a value of 3.30 × 10^{16} e.v./g./min. is obtained for the rate of energy dissipation in the butane. The absolute radiation yields calculated from this figure are given in Table II.

Possible Importance of Self-radiolysis.—Since the addition of carrier materials results in a 50-fold dilution of the activity and since only a small fraction of the total activity appears in any particular component, it is necessary to use high specific activity radioiodine, at least in the case of experiments carried out in more dilute solutions. The possibility therefore arises that appreciable reaction will result from self-radiolysis of the sample due to the radiations from I^{131}. With this in mind, contact between the radioiodine and the liquid butane was kept to a minimum and, in general, the standing periods were not more than a few days. However, some estimate of the extent of this self-radiolysis is in order. In these experiments the activity level was approximately 0.1 millicurie per gram of sample. Taking the average absorbed energy per disintegration as 0.2 Mev., it is estimated that the I^{131} dissipates energy in the butane at the rate of 6.4 × 10^{16} e.v./g./day. This compares with a total energy deposition in the sample of the order of 3.3 × 10^{19} e.v./g. from the Co^{60} field. It is seen, therefore, that the effects of self-radiolysis are negligible here (~1%) but that they must be taken into account if one were to use an appreciably higher specific activity material.

Product Distribution.—The distribution of activity among the various products is given in Table I along with the material balance obtained by comparing the sum of the total activities found for each component to that of the mixed carrier sample. Essentially all of the activity is accounted for. The radiation yield for each individual component is given in Table II.

Effect of Iodine Concentration.—The radiation yields for ethyl, *n*-propyl, isopropyl, *sec*-butyl and *n*-butyl iodides are essentially independent of iodine concentration over the region studied. The observed yield of activity in the methyl iodide shows a considerably greater scatter than appears in any other of the iodides. This scatter makes determination of the functional dependence of the radiation yield upon iodine concentration somewhat elusive although it is believed that here too the yield is substantially independent of iodine concentration and has a value of about 0.4.

The cause for the scatter in the case of methyl iodide is unknown but apparently does not originate in the fractionation procedure since quite adequate fractionations have been obtained in other investigations.[7,8,11,12] Although the higher iodides exhibit a negligibly small rate of thermal exchange

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with radioiodine, methyl iodide, especially if impure, reacts at a considerably higher rate. Because of the low fractional reactions in these radiolysis studies, several tenths of a per cent. pickup of the activity by the methyl iodide carrier would amount to an appreciable increase in the apparent yield. It is probable, therefore, that the high yields of methyl iodide in the experiments at 0.0112 and 0.0230 *M* are due to some defect in the experimental procedure, possibly to reaction of radioiodine with an impurity present in the batches of carrier used in these particular experiments. Two experiments in which only methyl iodide was determined were carried out as specific checks on the methyl iodide yield and are also reported in Table I. Here the activity was separated as quickly as possible after addition of the sample to the carrier mixture to minimize any possible exchange.

Discussion

Although the amounts of the simpler alkyl iodide products are independent of concentration, it is seen that the radiation yield of total combined iodine increases in the concentration region studied from 5.6 to about 9. This observed increase is due to the formation of methylene iodide and more importantly to the formation of other high boiling products and is about twice as large as that found in similar studies with cyclohexane.[6] The constancy in the yields of monoiodide products is a somewhat surprising fact in view of the drop in the hydrogen yield resulting from these scavenger concentrations in the case of cyclohexane.[13] The radical products are unaffected by changes in the physical and chemical processes which cause the drop in hydrogen and increase in diiodide yields and, therefore, appear to be formed in the early stages of the radiation decomposition. Of particular importance is the indication from the constancy of the *n*-butyl and *sec*-butyl yields at high iodine concentrations that production of butyl radicals by abstraction reactions such as

$$H\cdot + C_4H_{10} \longrightarrow H_2 + C_4H_9\cdot \qquad (1)$$

is unimportant. It seems likely therefore, as has also been indicated in other studies, that the observed hydrogen gas is produced by an ultimate molecule reaction rather than by an abstraction reaction similar to 1.

The increase in diiodide products interestingly occurs in the concentration region of 10^{-2} *M* where it has been shown[13] that the molecular hydrogen yield drops. Williams and Hamill[14] have called attention to the importance of electron traps in this region of solute concentration and have suggested that iodine can act as an electron scavenger. This change in the primary species might permit the production of stable diiodide products by a direct radiation-induced reaction between the iodine and the hydrocarbon.

Relative Importance of Various Modes of Fragmentation.—The interaction of radiation with matter produces as primary fragments both radical and ionic species, the chemical importance of each being as yet undetermined. Although there has been a theoretical indication that charge neutralization takes place in the case of liquids before chemical reactions come into play,[15,16] recent work with the mass spectrometer has shown that the cross-sections for ion–molecule reactions are very large[17] and has indicated that these reactions may be important intermediary processes in the radiation chemistry of liquids.[18] The present study includes at least one indication that ionic mechanisms play an important role. If the radiation decomposition involves radicals but not ions, equivalent amounts of methyl and *n*-propyl radicals would be expected to result from the radiolysis of butane. It is seen here that the yield of *n*-propyl iodide is only one fourth that of methyl iodide. This low value can scarcely result from the thermal dissociation of propyl radicals since if such were an important process, the measured propyl iodide yield should be dependent on the concentration of iodine. It thus seems necessary to include in the mechanism some step other than simple homolytic dissociation of butane molecules into radicals.

Although comparison of results obtained from the mass spectrometer and from the irradiation of liquid systems cannot be simple, it is worth noting that the most abundant ion in the mass spectrum of butane is $C_3H_7^+$ and that the ratio $C_3H_7^+/CH_3^+$ is about 17. The ratio of the complementary radicals will thus be presumably considerably larger than unity in qualitative agreement with data of Table II. Gevantman and Williams[9] have pointed out that such a complementarity is observed between the relative abundance of radicals detected by radioiodine and of ions formed in the mass spectrometer in the case of propane, *n*-pentane, and neopentane vapors. Present data on liquid butane are quite analogous to the results of Gevantman and Williams on pentane vapor but show no correlation with their results for butane vapor.

It is seen that the ratio for formation of *sec*-butyl and *n*-butyl radicals is about two to one, although the ratio of primary to secondary hydrogen atoms is about three to two. A similar preferential rupture for particular bonds has, of course, already been shown in the case of alkyl iodides, alcohols and carboxylic acids. This appears to be in accord with semi-quantitative theories for mass spectra of polyatomic molecules,[19] where it is postulated that decomposition occurs only after the positive ions have undergone a number of vibrations which effectively distribute the energy throughout the whole molecule.

The carrier distillation method employed here is quite tedious and of limited scope due to the difficulties of separating the iodides. However, the introduction of simpler vapor chromatographic proce-

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dures now available should make the radioiodine detection method more generally useful. Since it has been shown recently that carrier-free mixtures of the organic bromides can be separated on partition columns,[20] use of this technique may avoid difficulties due to failure to add proper carrier components. It is hoped that extension of these studies may reveal much more in the way of the fine structure of the radical spectrum produced by radiation.

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JERSEY CITY, NEW JERSEY
UPTON, LONG ISLAND, N. Y.

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Evaluation of Inductive and Resonance Effects in Reactivity. II. Thermodynamic Properties of Hydrogenation of Non-conjugated Olefins, Aldehydes and Ketones[1]

BY ROBERT W. TAFT, JR., AND M. M. KREEVOY

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The effect of unconjugated (α,β-saturated) substituents on the enthalpies of hydrogenation of mono- and *trans*-disubstituted ethylenes, $\Delta\Delta H^\circ$, and on the free energies of hydrogenation of carbonyl compounds, $R_1R_2C{=}O$, $\Delta\Delta F^\circ$, are found to follow with acceptable precision eq. 2: $\Delta\Delta H^\circ$ (or $\Delta\Delta F^\circ$) $= (\Sigma\sigma^*)\rho^* + (\Delta n)h$. This empirical relationship is suggested by and is correlated with the hypothesis that polar and hyperconjugative effects of the substituents contribute approximately additively to give the observed effect on the thermodynamic property. This hypothesis unifies diverse observed effects of substituents with theory. An important polar contribution to the thermodynamic properties for these reactions is expected in view of the change from the sp^2 to the sp^3 valence state of carbon which accompanies the hydrogenation. Evidence is obtained that hyperconjugation stabilization is much less susceptible to electron demand at the reaction center than is stabilization by inductive electron-release. The hyperconjugation stabilization per α-hydrogen atom in an open chain olefin or carbonyl compound is found to be about 0.5 kcal./mole.

The effect of alkyl substituents on the enthalpies of hydrogenation of olefins has been commonly attributed to hyperconjugation of the group with the C–C double bond.[2,3] If the entire effect of the substituent on the enthalpy of hydrogenation is attributed to hyperconjugation or conjugation in the olefin, the resulting hyperconjugation energies obtained for alkyl groups appear to be unreasonably large compared to the conjugation energies obtained for α,β-unsaturated substituents.[4]

Adkins and students have determined the free energies of hydrogenation of numerous aldehydes and ketones in dilute toluene solutions at 60°.[5] Hyperconjugation of alkyl substituents with the carbonyl group is reasonably expected to make at least as important contribution to these hydrogenation equilibria as those for olefin hydrogenation. However, the effects of alkyl groups on the free energies of hydrogenation of aldehyde and ketones do not show a distinct hyperconjugation order. In fact, conjugation effects of unsaturated groups on the free energies of hydrogenation are frequently not (or only slightly) discernible.

The hydrogenation of double bonded compounds is accompanied by a marked decrease in the intrinsic electronegativity of the atoms at the double bond.[6] This results from the fact that the sp^2 valence state of a given atom is appreciably more electronegative than the sp^3 state. Rates and equilibria for reactions which involve a substantial change in the electron demand at the reaction center show large susceptibilities to the electron attracting and releasing powers of substituent groups. That is, polar effects of substituents are large for reactions of this kind.

Important inductive, as well as hyperconjugation, effects are therefore expected to contribute to the observed effects of substituents on the enthalpies and free energies of hydrogenation of olefins, aldehydes and ketones.

In paper I it was shown that the very large effects of substituents on the rates of hydrolysis of diethyl acetals and ketals (of non-conjugated aldehydes and ketones) are correlated in an approximately quantitative manner by an equation which attributes the total effect of the substituent on the free energy of activation to the sum of independent inductive and hyperconjugation effects.[7] The acid-catalyzed rate constants in this reaction series follow with acceptable precision the equation

$$\log (k/k_0) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (1)$$

where $\Sigma\sigma^*$ is the sum of the polar substituent constants, σ^*, for the substituents, R_1 and R_2, of the acetal or ketal of the general formula $R_1R_2C(OC_2H_5)_2$. These polar substituent constants were ob-

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[1] The work herein reported was carried out on Project NR055-328 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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