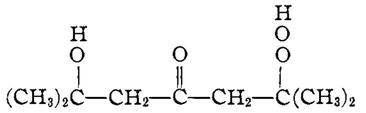
solved. Thus, despite the apparent inability of a peroxy radical in the 2-position to remove a hydrogen atom in the 6-position—at least with any facility—there is considerable indication that removal of hydrogen from the 4- and 5-positions is occurring with considerable regularity. In this connection the tentative identification of a crystalline compound



$(CH_3)_2C(OH)-CH_2-C(=O)-CH_2-C(OOH)(CH_3)_2$

suggests the possibility of a "zipper" effect in the oxidation of certain linear hydrocarbons. The amount of this compound was, however, too small to suggest that such an effect would be important in any but special situations.

When 2,3-dimethylpentane is oxidized and the peroxides reduced, 2,3-dimethyl-2-(and 3)-pentanol are the principal and almost equally important products. It is significant that 3,4-dimethyl-2-pentanone-4-ol, which is the only reduction product which would be expected by a β-oxidation mechanism, is the most important of the remaining products retaining the original carbon skeleton. α-Attack by a peroxy radical seems to be of no significance.

In view of the foregoing results it seems reasonable to relate much of the formation of keto-acids, lactones, etc., in conventional paraffin oxidation to intramolecular chain propagation. However, no such extensive intramolecular reaction has been observed in the oxidation of the normal paraffins as was found for these branch chain hydrocarbons. Therefore, it is concluded that the well recognized effect of a gem-dimethyl grouping[7] in favoring ring closures is important here in intramolecular attack by peroxy groups.

Acknowledgment.—The author wishes to acknowledge particularly helpful discussions with Drs. H. E. De La Mare and D. E. Winkler.

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(7) P. D. Bartlett, *J. Chem. Ed.*, **30**, 27 (1953).

EMERYVILLE, CALIF.

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

Free Radicals from the Heterogeneous Decomposition of Butane[1]

BY SYDNEY W. FLEMING AND K. A. KRIEGER

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A method which provides information about the nature of certain adsorbed intermediates is described. Essentially the method consists in observing the decomposition of a hydrocarbon (butane) into free radicals on a heated wire acting as a catalyst. The reaction is carried out at pressures of 1–2 μ in a vessel whose walls are coated with radioactive iodine. The alkyl iodides formed are separated and their activities measured. Catalyst temperatures ranged from 305 to 1490°. Both aluminum (oxide) and tungsten catalysts produce free radicals ranging in complexity from methyl to *sec*-butyl. The radicals formed depend upon the catalyst used and on the temperature. Platinum produces no free radicals under these conditions.

Introduction

A major problem in catalysis is that of discovering the nature of the intermediates whose formation is critical in determining the course of the reaction. In the case of heterogeneous catalysis the methods of studying the intermediates are especially limited, owing to the necessary presence of a catalyst, most often a solid, on whose surface the critical intermediate is formed, and which greatly interferes with the usual methods of observation. In seeking a solution to this difficulty some success has been attained by the use of infrared spectroscopy, which, in suitable circumstances, is able to detect alterations in chemical bonds attendant on adsorption.

The present paper is an attempt, along quite different lines, to approach the observation of adsorbed intermediates. Unfortunately, the method is not quite direct, as the description will show, but it does apparently succeed at least in detecting certain immediate products of desorption, before their nature has been changed by subsequent reaction.

The results reported here are limited to a single reactant and three catalysts, and it is difficult with these limited data to make with certainty any very broad generalizations. The collection of future data, with more varied reactants and catalysts, is expected to remedy this defect. Additional work utilizing this method is in progress in this Laboratory, but this report is made now in the hope that others may find the technique useful.

Experimental

Briefly, the method involves production of free radicals by decomposition of butane on catalysts in the form of metal wires and trapping of the free radicals released by the catalyst into the vapor phase by means of a radioactive iodine mirror, followed by fractional distillation and determination of the activities of individual fractions. These activities give the relative quantities of the alkyl iodides formed from the original free radicals trapped by the mirror.

Apparatus.—The experimental apparatus, shown in Fig. 1, consisted of a reaction chamber, L, with a wire catalyst suspended in the center and equipped with electrical connections for heating the wire. Associated apparatus was provided for metering butane into the reaction chamber at the very low rates required. The mirror was formed on the walls of the reaction vessel, and in order for free radicals formed on the wire to reach the wall without suffering collision with butane molecules, the butane pressure was kept between 1 and 2 μ, giving a mean free path on the order of the tube diameter of 5 cm.

During each run the vessel containing the iodine mirror was maintained at Dry Ice temperature. At the end of each run the reaction vessel was warmed to room temperature to allow the product along with the excess free iodine to dis-

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(1) Based on a thesis submitted to the University of Pennsylvania, 1954 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

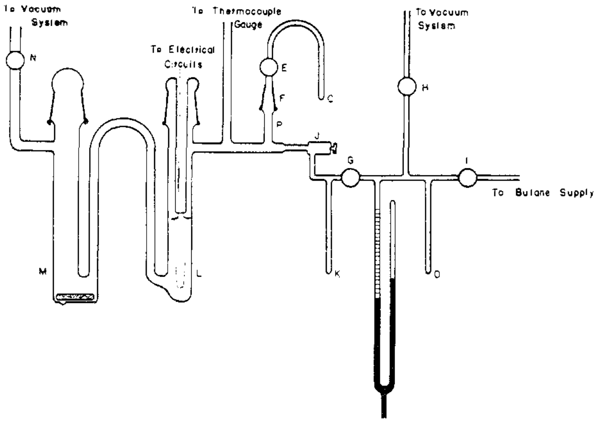

Fig. 1.

til over into M, held at liquid air temperature, after which the carrier alkyl iodides were added to the mixture. The unreacted free iodine was removed by extraction with aqueous sodium sulfite and the alkyl iodides removed, dried and distilled. Following distillation, the activities of the individual fractions were determined in a counting device designed to accommodate the tube in which the fractions were collected. This device consisted of six Nuclear Instrument and Chemical Corp. Type D76 Geiger-Mueller tubes held vertically and arranged in a circle nearly touching each other. A space of just over one-half inch in the center of these tubes was available to accommodate the fraction tube, which was supported so that the sample itself was nearly centered in the active counting space. With this arrangement, counting efficiency was approximately independent of exact sample shape and placement so that all of the many sample tubes used were effectively identical.

Reagents.—The radioactive iodine was obtained from The Atomic Energy Commission, Oak Ridge, Tennessee. The solution as received was diluted so that each ml. contained about 1 millicurie of activity, and appropriate amounts of this solution were withdrawn for each run.

The butane was research grade *n*-butane obtained from Phillips Petroleum Company. This butane was 99.78 ±0.08% pure and was used directly from the cylinder as received.

The alkyl iodides came from Eastman Kodak Company, Mathieson and Bell, and Paragon Laboratories. In each case, the iodides were distilled once through a glass packed column about one meter long before being used. In the case of ethyl iodide, where special purity was required, the material was distilled twice and further purified by shaking it with red phosphorus and by passing it through a column of activated silica gel. Blank runs were made on each batch of ethyl iodide to make sure that the blank activity was suitably low in each case.

The No. 30 platinum wire used for filaments was obtained from Bishop Platinum Company. The No. 24 soft-drawn aluminum wire of approximately 98% purity was obtained from Arthur H. Thomas Company, and was treated by immersion in dilute KOH solution before initial use.

The tungsten filaments were cut intact with their attached leads from 150 watt electric light bulbs made by the Westinghouse Electric Corporation, and were used without treatment.

Procedure.—Approximately 2 mg. of iodine having an activity of about 0.5 millicurie was distilled into finger C at liquid air temperature, after which the finger was assembled into the main apparatus as shown in Fig. 1. The entire apparatus then was evacuated thoroughly, after which C was allowed to warm slowly as a vessel of liquid air was being raised around reaction vessel L. In this way a fairly uniform mirror of iodine was deposited on the walls of L; the liquid air was replaced by a Dry Ice–acetone mixture before proceeding with the run.

Butane was admitted during each run from finger K, held at the melting point of methylcyclohexane, by means of needle valve J at such a rate as to maintain a pressure of 1 μ in vessel L as recorded by a thermocouple vacuum gage. Throughout the run vessel M was held at liquid air temperature to trap any materials, including unreacted butane, that might escape from L.

At the conclusion of a run, stopcock N was closed and vessel L warmed to allow all reaction products to condense on the bottom of vessel M. The cap to M was then removed and 12 ml. of ethyl iodide carrier[2] and an aqueous sodium sulfite solution containing small quantities of potassium iodide and sodium bicarbonate was added. After stirring and removing this aqueous layer, followed by several washings, 12 ml. each of propyl and butyl iodides were added, and the organic layer removed by means of the pipet shown in Fig. 2. The 12 ml. of carrier methyl iodide was added at this point, and the mixture was allowed to stand over anhydrous magnesium sulfate overnight.

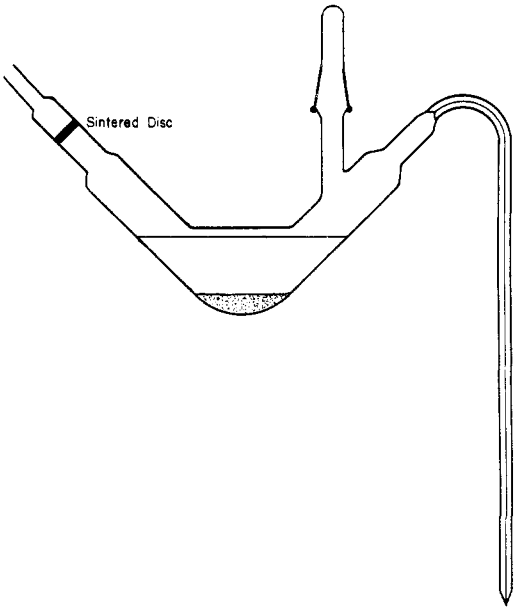

Fig. 2.

The liquid was charged into the still pot for distillation by tilting the pipet so that the liquid ran out through the sintered glass disc which retained the drying agent; the process was hastened by applying gentle air pressure over the liquid.

Distillations were made in a conventional glass-packed column of approximately 12 mm. inside diameter and 1 meter length. Take-off was controlled by a timer-operated solenoid valve. Two-ml. samples were collected in calibrated tubes made from 12-mm. Pyrex tubing.

In each run 12 ml. each of methyl, ethyl, *n*-propyl and *n*-butyl iodides were used as carriers, so that with normal losses, five samples of 2 ml. each could be obtained for each carrier after distillation. In each distillation the methyl and ethyl fractions were taken off at atmospheric pressure, after which 20 ml. of *n*-amyl iodide was added to serve as a chaser, and the pressure reduced to approximately 210 mm. before continuing the distillation. At this pressure the maximum temperature reached was about 112° for the amyl fraction, so that decomposition was minimized. The activity of each fraction was determined immediately after removal from the column; counting was usually complete before the subsequent fraction was ready to be counted. When necessary, suitable correction was made for radioactive decay.

Results and Discussion

The results of several of the runs reported are presented in the form of graphs on which are plotted the activities of the fractions collected and the corresponding boiling point curves. The various fractions are identified across the bottom of each graph, and the boiling point curves serve to define

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[2] When a mixture containing all alkyl iodides was added at this point, high spurious activities were found in the methyl iodide fraction. Addition of ethyl iodide only at this time, followed by the others later, resulted in lower blanks than any other method tried.

the transitions between them. The boiling points are shown in °C. along the right-hand ordinate, with the jagged line indicating the point at which the distillation pressure was reduced from atmospheric to approximately 210 mm. Relative activities are plotted along the left-hand ordinates, the highest activity found in a given run being taken as unity and all others in that run being plotted as fractions of it. The values used for calculation of this relative activity were total activities uncorrected for the levels found in the blank runs, and the absolute value for the highest activity is shown in counts per minute (c.p.m.) in each graph. The activity labeled R in the graphs was that of a 2-ml. sample of the pot residue at the end of the distillation.

Blank Runs.—Blank tests of various kinds were made as follows.

Pure lead tetraethyl vapor was passed at a low pressure through the reaction chamber, a short section of which was heated to 200°. A platinum filament heated to approximately 400° was employed to make decomposition more nearly complete. An iodine-131 mirror of the usual type was entirely consumed in about an hour, and the activity appearing in the ethyl fraction was extremely high, demonstrating that when free radicals are present they can be detected. Results are shown in run 35, Fig. 3.

The appearance of radicals which were not in fact formed from butane by the action of the catalyst might have been simulated by: (a) exchange between free radioactive iodine and the alkyl iodides used as carriers; (b) exchange between labeled alkyl iodides and carrier iodides; (c) reaction between primary free radicals and the reactant (butane) or a second primary radical to form new (secondary) free radicals; (d) radiolysis of butane or carrier iodides before extraction of excess radioactive iodine.

That (a) did not occur to a significant extent (provided ethyl iodide only was added as carrier before the excess radioactive iodine was removed) was shown by blank runs, 29 and 44, Fig. 3.

These are the blanks which showed the highest and lowest activities, respectively, of all blanks run. It was at first thought that the activities observed in the blanks were caused by exchange, but this could not account for the butyl peak when only ethyl iodide had been in contact with radioactive iodine or significant concentrations of radioactive iodide ion. The other possibility was that the ethyl iodide underwent radiolysis by the high-energy β- and γ-rays emitted by iodine-131 itself. The work of a number of authors supports this conclusion.[3,4] A number of different materials were tried as the extracting medium, but carefully purified ethyl iodide was found to result in the lowest blanks.

As noted, the possibility of radiolysis of alkyl iodides cannot be entirely eliminated, but it is clearly at worst a minor source of radicals, insufficient to interfere with the observation of appreciable quantities of authentic free radicals.

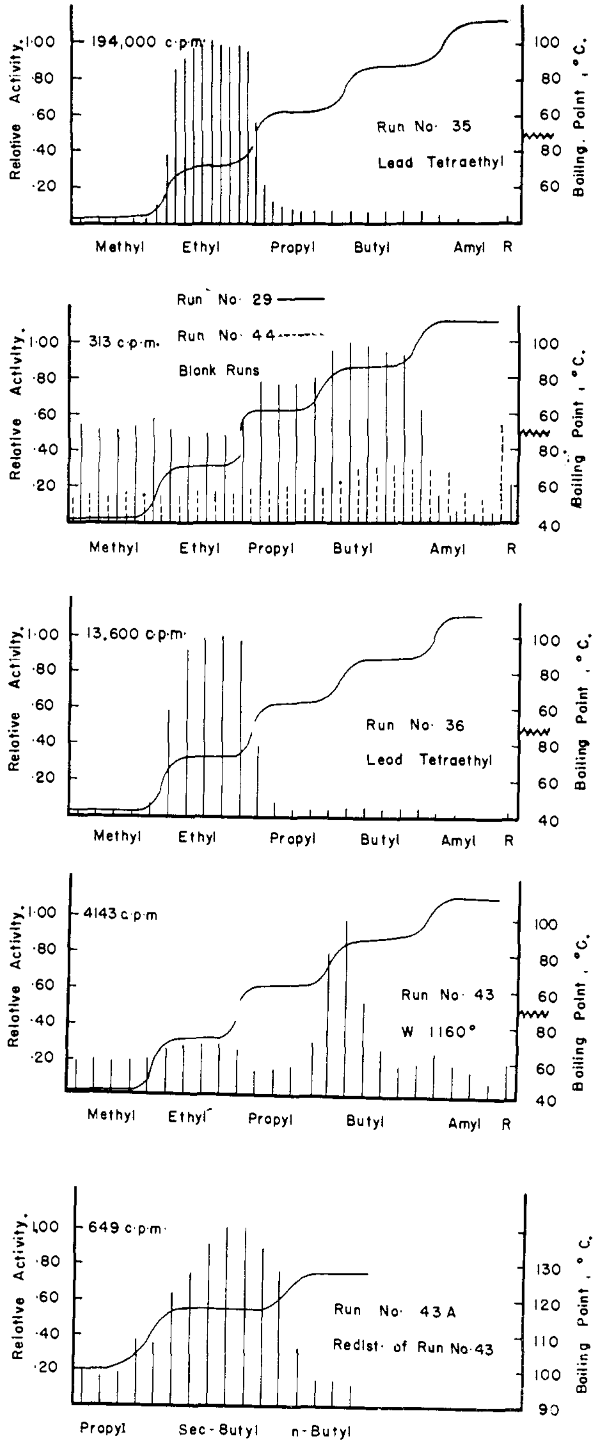

Fig. 3.

To make certain that no radiolysis of butane was occurring either during a run or after a run when all materials were distilled into the extraction vessel, run No. 44 was performed exactly as a normal run, except that the wire was left cold. After distillation the activities of all fractions were found to be considerably below the level of run no. 29, the standard reference blank.

Exchange between labeled and carrier alkyl iodides cannot occur to any considerable extent, as is

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[3] R. H. Schuler and W. H. Hamill, THIS JOURNAL, **74**, 6171 (1952).

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

TABLE I

Run	Filament material	Surface area, cm.^{2}	Temp., °C.	Length of run, min.	Moles of butane × 10^5	Apparent collision efficiency × 10^7			
						Methyl	Ethyl	*sec*-Butyl	*n*-Butyl
49	Al	40.1	305	250	14.5	0.8			
17	Al	9.1	360	80	3.7	39			
47	Al	6.2	430	270	16.7				7
50	Al	40.1	440	195	11.2	0.8		0.9	1
31	Al	6.2	540	60	3.1	4	8	7	
46	Al	6.2	540	210	12.2			8	
45	W	2.0	780	210	12(est.)		9		
41	W	2.0	820	210	12.9		10		
39	W	2.0	1125	160	10(est.)	25	54	37	
43	W	2.0	1160	230	13.2	10	16	37	
40	W	2.0	1200	190	12.1	38	85	20	
38	W	2.0	1335	140	3.6	16	13	6	
42	W	2.0	1490	70	2.3		35	26	16

shown by the existence of many cases in which a strong activity in one species is accompanied by very weak activities in others. Obviously extensive exchange would level off the peaks. Similar observations were recorded by Schuler and Hamill[3] and Gevantman and Williams.[4]

The possibility of reaction between butane and primary free radicals was eliminated by the following experiment. Immediately following run 35, in which lead tetraethyl had been introduced, an ordinary run was carried out using butane and a platinum filament at *ca.* 1300°. Traces of lead tetraethyl which had dissolved in the stopcock grease during run 35 were evolved and decomposed during the run to yield ethyl radicals. The results of the run (36, Fig. 3) show very clearly only ethyl radicals, so that it is evident that ethyl radicals do not react with butane, under the experimental conditions, to produce other radicals.

The reproducibility of the over-all results is not as good as might be desired. It is the opinion of the writers, however, that the lack of reproducibility shown in some runs (runs 40 and 43 represent the worst cases) is a result more of the variability of the temperature and condition of the catalyst than of the method of detection. The greatest uncertainty arising in attempting to interpret the results of butane decomposition over tungsten and aluminum wires is that of the temperature of the wires. This temperature was determined electrically before and during runs, and such measurements are subject to errors arising from changes in contact resistance during a run and to non-uniformities in temperature within a filament. Apparently for this reason some of the trends in the data appear to be contradicted by individual runs, and some runs show results which appear to be composites of higher and lower temperature runs.

Platinum Catalyst.—In none of the runs made with platinum wires were significant quantities of free radicals detected, and so these runs are not individually reported. The temperatures used ranged from 400 to 1200°, and platinized platinum wires as well as smooth wires were tried. The negative results obtained indicate that if decomposition occurred, it proceeded through a mechanism not involving free radicals, or by a mechanism in which free radicals did not leave the surface of the wire. It would seem reasonable to assume that the principal products of any decomposition that might have occurred were unsaturated compounds rather than free radicals.

Tungsten Catalyst.—The results of all runs performed with tungsten and aluminum catalysts are presented in Table I. The apparent collision efficiency shown in this table is the ratio of the number of radicals found to the number of butane molecules colliding with the catalyst, and is therefore a measure of the relative tendency of the catalysts to form radicals of the kind shown.

Examination of Table I will show that the tungsten filaments produced ethyl radicals at all temperatures, and that at the higher temperatures secondary butyl radicals were produced in significant amounts. In none of the runs was secondary butyl iodide added as a carrier; this radical showed up between the propyl and *n*-butyl fractions as a sharp peak rather than a broad plateau. Figure 3 (run 43) shows the boiling point and activity curve obtained, and a subsequent redistillation (run 43A) of a small cut of the secondary butyl peak with the addition of carrier secondary butyl iodide. This redistillation supports the identification of the peak as due to secondary butyl radicals, although isobutyl radicals remain an unlikely possibility.

Aluminum (Oxide) Catalyst.—The results of the aluminum runs may be summarized by saying that at temperatures around 300° only methyl radicals were detected in significant amounts, while at somewhat higher temperatures (430–440°) only normal butyl radicals (and some indication of secondary butyl) were detected, and at the highest temperatures (approximately 540°) principally secondary butyl radicals were detected.

Conclusions

In spite of some irregularities in individual runs, some generalizations emerge from the data as a whole.

(a) The character of the products *in general terms* is a function of the temperature. Thus, both Al and W produce chiefly products of C–C bond scission at lower, and of C–H bond scission at higher, temperatures. This result is to be expected on purely energetic grounds, and it is noted that the catalytic effect of these metals is not sufficient to produce deviations from the expected result. However, the failure of products of C–C bond scission to appear in the case of Pt may mean that C–H bond scission occurs to such an extent, even at low temperatures, that unsaturates (which would not be detected in this procedure), rather than free radicals, are formed. Unfortunately we can produce no direct evidence for this process.

(b) The character of the products *in detail* is affected by the catalyst used, and hence it is clear that the effect being observed is not purely thermal. Individual differences have been pointed out in the preceding section. An explanation for the apparent tendency of W to produce ethyl radicals and for Al to produce methyl radicals, at the lowest temperatures, for example, is not readily forthcoming, however.

(c) The favoring of those radicals which have been generally regarded as most stable is noted. Thus *sec*-butyl radicals in preference to *n*-butyl are observed at the highest temperatures. Whether the disappearance of *n*-butyl and the appearance of *sec*-butyl reflects a changing activity of the catalysts with temperature, or whether it is a result of isomerization of the *n*-butyl radicals originally formed is not entirely certain, but it should be noted that *n*-butyl radicals were observed in some runs and there is therefore some reason to suppose that the shift to *sec*-butyl is a property of the catalyst and not merely a result of isomerization.

The failure to detect propyl radicals of any kind in significant amounts is a striking result, especially in the face of quite high methyl activities, which suggest a 1,2 C–C bond scission. There appear to be at least three possible explanations for their nonappearance: (1) propyl radicals may be formed, along with methyl, but may remain adsorbed. Since the energy required to desorb a propyl radical would be expected to be little different from that for methyl, this assumption does not appear tenable; (2) propyl radicals may be formed but undergo decomposition into ethylene plus methyl radicals. A comparison of the energies of activation[5] for the reactions

$$C_3H_7\cdot \longrightarrow C_2H_4 + CH_3\cdot \qquad E = 20 \text{ kcal.}$$

$$n\text{-}C_4H_9\cdot \longrightarrow C_2H_4 + C_2H_5\cdot \qquad E = 23 \text{ kcal.}$$

$$n\text{-}C_4H_9\cdot \longrightarrow C_3H_6 + CH_3\cdot \qquad E = 23 \text{ kcal.}$$

leads to the conclusion (assuming equal frequency factors) that the ratio of the rate of decomposition of the propyl radicals from aluminum at 360° (run no. 17) to that of the decomposition of *n*-butyl radical from aluminum at 430° (run no. 47) is approximately

$$\exp\left(\frac{23{,}000}{703 \times 2} - \frac{20{,}000}{633 \times 2}\right) = 1.75$$

Since butyl radicals were readily detected in run no. 47 and methyl radicals in run no. 17, it appears that if propyl radicals had been produced in run no. 17 in quantities approximating the methyl radicals, they should have been detected easily. While it is recognized that errors in the temperature of the radicals leaving the wire, and in the values of the energies of activation for the radical decompositions, could affect this conclusion in a quantitative sense, it is improbable that some clearcut evidence for propyl radicals would not have been found if they are produced in quantities approximating methyl radicals. (3) The third possibility is that on aluminum two point adsorption takes place at the 2,3-positions, resulting in the formation of two methyl radicals and ethylene. Two point adsorption in the 1,2-position would yield ethylene and ethyl radicals, which are in fact observed at higher temperatures. Although there appears to be no firm ground upon which the preference for 2,3-adsorption at low temperatures and 1,2 at high can be explained, all of the data on aluminum which correspond to C–C scission conform to two point adsorption, and this hypothesis is the one most satisfactory at present. It is perhaps worth noting that on tungsten also the results of C–C scission are explainable on the assumption of 2,3-adsorption.

(d) The appearance of the relatively complex *sec*-butyl radical at high temperatures is surprising since the extent of decomposition would be expected to increase with increasing temperature. The most likely explanation is that the residence time on the catalyst decreases rapidly with temperature, but we have no direct experimental evidence of this.

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[5] S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 319 (1951); 172 (1951)