

Nitrogen Analysis.—The nitrogen contents of the isolated samples were determined by the method of Cavett.²² Each recorded nitrogen value represents the average of at least two independent determinations.

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Summary

1. Glutamic acid hydrochloride was isolated from hydrolyzed casein by six different procedures. The percentages of *d*-isomer in the isolated samples varied from 2.5 to 6.2%.

2. The isolations were repeated, using this time a casein hydrolyzate to which had been added a

(22) J. W. Cavett, *J. Lab. Clin. Med.*, **17**, 79 (1931).

known amount of *d,l*-glutamic acid. The methods yielding samples having *d*-isomer contents closest to the theoretical content were the pyrrolidone-carboxylic acid procedure and the cuprous oxide procedure. Two modifications of the Foreman procedure yielded samples containing, respectively, 76–89 and 82–96% of the theoretical content of *d*-isomer. The poorest percentage yields of *d*-isomer were obtained with the zinc oxide procedure.

3. Methods for isolating glutamic acid by the pyrrolidone-carboxylic acid procedure and the zinc oxide clarification procedure, and modifications of the barium salt and butyl alcohol extraction procedures are described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Products from the Wurtz Reaction and the Mechanism of their Formation¹

BY ALFRED SAFFER AND T. W. DAVIS

The combination of methyl radicals with each other does not seem to occur under conditions where other combinations proceed readily.² The symmetrical approach of two methyl groups according to calculations of Kimball³ and of Kassel⁴ leads to a product of very short life. There is a possibility that methyl and ethyl radicals, being unlike, may combine more readily than like radicals, in which event the cross combination would result in a preponderant formation of propane, for example, in a Wurtz synthesis involving a methyl and an ethyl compound. The Wurtz reactions seem to offer a way to generate free radicals in any desired proportions so that one may study the relative probability of particular free radical combinations. The results of such a study are reported in this paper.

Von Hartel and Polanyi⁵ found the reaction of methyl iodide with sodium vapor to proceed with zero energy of activation, and the reaction ought to go at every collision, therefore, regardless of the temperature. But below 300°, there is no

measurable reaction because of the low vapor pressure of the metal. Above 300° with pressures of iodide in the neighborhood of 100 mm., the reaction with methyl or ethyl iodide proceeds at a convenient rate. Our experiments were conducted at 320° and in the absence of solvent because the compounds used as solvents in the ordinary Wurtz syntheses often enter into the reactions.⁶ Consequently, in undertaking a study of mixed free radical reactions, we have found it convenient and desirable to depart markedly from the conventional details of the Wurtz synthesis.

Experimental

Method.—The apparatus for this study was used in the following way. About nine grams of sodium was placed in the large bulb of the addition tube, D, and the open end, E, was sealed off. The system was evacuated and the sodium melted by heating with a flame until it flowed into the lower and smaller bulb, where it was further melted and allowed to run into the reaction vessel, C.

During a run, the sodium was kept at 320° by means of the furnace, B. The reactant vapors were introduced by dropping liquid from the

(1) Presented at the Atlantic City meeting of the American Chemical Society, Sept. 10, 1941. Original manuscript received November 5, 1941.

(2) (a) Davis, Jahn and Burton, *THIS JOURNAL*, **60**, 10 (1938); (b) H. A. Taylor and M. Burton, *J. Chem. Phys.*, **7**, 675 (1939); (c) Burton, Taylor and Davis, *ibid.*, **7**, 1080 (1939); (d) A. Gordon and H. A. Taylor, *THIS JOURNAL*, **63**, 3435 (1941).

(3) G. E. Kimball, *J. Chem. Phys.*, **5**, 310 (1937).

(4) L. S. Kassel, *ibid.*, **5**, 922 (1937); cf. E. Teller, *Annals New York Academy of Sciences*, **41**, 173 (1941).

(5) H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

(6) Hüchel, Kraemer and Thiele, *J. prakt. Chem.*, N. F. **142**, 207 (1935); W. E. Bachmann and T. H. Clarke, *THIS JOURNAL*, **49**, 2089 (1927); A. A. Morton and F. Fallwell, *ibid.*, **59**, 2387 (1937); R. B. Richards, *Trans. Faraday Soc.*, **36**, 956 (1940); Whitmore, Popkin, Bernstein and Wilkins, *THIS JOURNAL*, **63**, 124 (1941); P. Schorigin, *Ber.*, **41**, 2711 (1908); A. A. Morton and I. Hechenbleikner, *THIS JOURNAL*, **58**, 2599 (1936).

dropping funnel, A, into the trap maintained above 100°. The vapors passed into the reaction vessel, spattering molten sodium over the walls. The alkyl iodide remained in contact with the sodium for ten minutes at a pressure of about 200 mm. Then on opening stopcock F, the products and unreacted iodide were drawn over into trap G, which was cooled in liquid nitrogen. This batch treatment was continued until enough halide had been sent through the apparatus in the course of several hours to produce on complete reaction an anticipated two liters of gaseous product, but under such circumstances reaction was only 10 to 40% complete as determined by Volhard titration of the sodium iodide formed.

The gaseous products volatile at liquid nitrogen temperatures were removed by a mercury piston and analyzed in a gas analysis apparatus of the Orsat type. The condensed material was warmed in turn to -131, -78 and -45° and the vapors released at the several temperatures were pumped off for analysis. The following table shows the products withdrawn from the condensate at the several temperatures.

TABLE I

FRACTIONATION OF PRODUCTS FROM REACTION MIXTURES

Refrigerating agent	Temp., °K.	Products released from mixture			
Liquid nitrogen	77	H ₂	CH ₄		
<i>s</i> -Butyl chloride mush	142	CH ₄	C ₂ H ₄	C ₂ H ₆	(C ₂ H ₂)
Dry-ice + toluene	195	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
Chlorobenzene mush	228	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀

The gas analyses were carried out in the usual way. The unsaturated hydrocarbons were dissolved in fuming sulfuric acid. The hydrogen (which appeared only in the fraction uncondensed by liquid nitrogen) and saturated hydrocarbons were estimated by burning with excess oxygen. It was assumed in compiling the data that the unsaturated components in any sample of gas had the same average number of carbon atoms per molecule as the saturated gases in the same sample, for the boiling points of unsaturated hydrocarbons are fairly close to the boiling points of the corresponding alkanes. Complete identification of the alkenes could be accomplished by catalytic hydrogenation of the samples followed by combustion and carbon dioxide determination but, since the proportion of these products is so low, the more lengthy procedure was not adopted.

The results of the parallel analyses of gas from the reaction mixtures, as recorded in Table III,

indicate the general consistency of the analytical results. To check further on the gas analysis methods, a mixture of tank gases was made up, mixed with about the quantity of methyl iodide used in our experiments and was fractionated in the usual manner. The tank gases were themselves analyzed before use. The results appear in Table II. There is clearly some uncer-

TABLE II
ANALYSES OF KNOWN GAS MIXTURES

Gas	Mixture I		Mixture II	
	Taken, ml.	Found, ml.	Taken, ml.	Found, ml.
C ₂ H ₄	6	6		
C ₂ H ₆	191	192		
C ₃ H ₆	18	16	9	9
C ₃ H ₈	91	93	168	146
C ₄ H ₈	1	5	2	9
C ₄ H ₁₀	96	62	148	146
Total	403	374	327	310

tainty, amounting to about 15 to 30 ml. total, in the butane and propane figures. This arises largely from the solubility of these heavier gases in the methyl iodide, from which they cannot be completely recovered. The magnitude of the uncertainty, however, is not so large as to modify seriously the interpretation of the reaction.

The consistent trends in the values of *n* in successive samples of gas drawn from the various mixtures give basis for confidence in the combustion methods for analyzing the heavier hydrocarbons, where *n* is the average number of carbon atoms per molecule of alkane gas. With pure propane or pure butane, combustion gave the expected values of 3 and 4, respectively, for *n*.

Materials.—Methyl and ethyl iodides to be used in the experiments were prepared by treating the corresponding alcohols with red phosphorus and iodine. The crude products were dried over calcium chloride and fractionally distilled. Their final boiling points of 42.2–42.7° and 71.5–72.1° are in agreement with accepted values.

Results

The analyses of the products secured from typical reactions of sodium with methyl iodide and ethyl iodide, both singly and in equimolecular mixture, are shown in Table III.

The large amount of methane from the methyl iodide is relatively unexpected as is the appearance of hydrogen, methane and propane in the gases from the ethyl compound. We have noted the formation of carbon in all of these experiments.

TABLE III

DISTRIBUTION OF PRODUCTS FROM WURTZ REACTIONS

Halide used Expt. no.	CH ₃ I 20	C ₂ H ₅ I 14	CH ₃ I + C ₂ H ₅ I 15	CH ₃ I + C ₂ H ₅ I 24
% H ₂	7.0	5.5	2.3	4.5
% CH ₄	64.1	3.9	42.7	42.9
% C ₂ H ₄	1.9	12.7	8.3	6.8 ^a
% C ₂ H ₆	27.0	51.1	20.3	19.9
% C ₃ H ₆		2.7	1.7	0.8
% C ₃ H ₈		15.2	16.1	12.5
% C ₄ H ₈		1.3	0.9	0.8
% C ₄ H ₁₀		7.6	7.7	11.8
Total gaseous products, ^b ml.	591.2	226.9	666.2	1231.5
Black residue, mg.	96.4	35.2	93.4	173.4
NaI formed, g.	6.290	2.255	7.173	12.71
% reaction	23.5	8.4	26.8	47.5

^a In this experiment acetylene was determined by absorption in ammoniacal silver nitrate solution. It made up 1.3% of the sample. This is included in the figure for % C₂H₄. ^b At S. T. P.

When all the volatile products had been distilled from the reaction vessel, methyl alcohol was added to the residual sodium iodide and excess sodium. The alcohol extract was always observed to contain much suspended material resembling carbon in appearance. This product was not introduced as an impurity in the sodium, for sodium melted into the apparatus, but not exposed to the halide vapors, yielded no carbon at all. Several of the black suspensions were filtered and the insoluble material was dried and weighed. The product had no observable solubility in ethyl alcohol, diethyl ether, tetralin, acetone or benzene and certainly is not to be confused with methylene polymer.

The carbon and hydrogen contents of some of the dried carbon samples were determined in a micro-combustion apparatus.⁷ The ratio of the two elements varied fairly widely, not only from specimen to specimen, but different samples from a single specimen were sometimes in bad agreement with each other. The ratios varied from C_{0.8}H₁ to C₄H₁. Evidently the carbon had adsorbed fairly large and variable amounts of hydrocarbon gases.

While the color of iodine vapors was not observed in any of our experiments, a dark liquid, not easily volatile, condensed in the leads above the reaction vessel. This fluid probably consisted of polyiodide containing some dissolved iodine. The excess and unreacted halide collected with the reaction products was distilled after the

(7) We are indebted to Dr. R. Bruce Van Order for these analyses.

hydrocarbon gases had been removed for analysis. While the material boiled at the temperature of the original reactants, there may have been present several per cent. of some higher iodide or hydrocarbon that would not be detected in our procedure.

In an effort to check on the completeness with which the chief reaction products were recovered, and to gain some idea of the nature of any missing products, a materials balance was set up for some of the runs. From the amount of sodium iodide formed, the quantities of carbon and hydrogen expected in the products may be computed, assuming further that in the mixture runs equimolecular amounts of the two halides enter into the original reaction. The detailed data for Experiments 15 and 24 appear in Table IV. The

TABLE IV

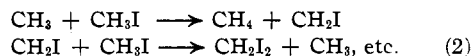
MATERIALS BALANCE IN WURTZ REACTIONS

Expt.	15	24
C expected, g.	0.861	1.526
H expected, g.	.190	0.339
C in gases	.664	1.229
H in gases	.161	0.305
C in black residue	.085	.119
H in black residue	.008	.0025
C recovered, %	87.6	88.5
H recovered, %	89.0	90.6

incomplete recovery of butane is sufficient to account for most of the hydrogen and carbon deficiencies, but possibly the formation of higher monohalides and hydrocarbons also contribute a little to the deficiency. Some of these products may arise from reactions like



or by hydrogen exchange reactions.⁸ These calculations are important in eliminating from the reaction scheme chain-producing reactions⁹ of the type



Were such chain reactions a source of appreciable amounts of free radicals, the hydrogen and carbon content of the recovered products would be more than equivalent to the sodium iodide remaining in the reaction flask, for if the dihalide formed in reaction (2) contains a greater percentage of iodide than the original reactant, its appearance

(8) A. O. Allen [THIS JOURNAL, 63, 708 (1941)] found these reactions to be of importance during the photolysis of acetone in the presence of propane.

(9) P. Fugasi and F. Daniels [*ibid.*, 60, 771 (1938)] observed no chains in ethyl bromide decomposition at 395°.

in the products would correspond to additional amounts of both carbon and hydrogen brought into the reaction but not accompanied by an equivalent production of sodium iodide. Other experiments not reported here indicate that the dihalides react about as readily with sodium as the monohalides at 320°.

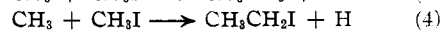
Mechanism

Methyl Iodide.—There is little doubt that the initial reaction involves the formation of sodium iodide and methyl radicals at the surface of the metal. Some of the radicals are doubtless held on the surface, but the instability of the sodium alkyls¹⁰ makes unlikely the confining of the reaction to the sodium surface.

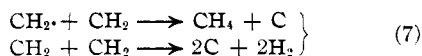
The most obvious second step in the reaction course is the union of the free radicals, but the multiplicity of products and their unexpected distribution indicates that such a picture is too simple, and a calculation of free radical concentrations shows that reactions between two alkyls are probably unimportant. Assuming the uniform production of the radicals and uniform distribution throughout the reaction vessel, and that the free radicals disappear in a chemical change with the alkyl iodide involving an energy of activation of 16 kcal., a steric factor of 0.1 and ordinary collision diameters, the partial pressure of the methyls will reach a steady state concentration of about 3×10^{-4} mm., when by contrast the pressure of halide is about 200 mm. If the bimolecular free radical reactions, either associations or disproportionations,¹¹ require an appreciable energy of activation, they will not contribute largely to the final products. On the other hand, the more probable free radical-molecule reactions lead to new free radicals which will meet halide molecules more frequently than any other species in the system. The occurrence of reaction chains of any considerable length, however, is not expected.⁸ The chains must be interrupted either by unimolecular decomposition to give unreactive fragments or by two-radical reactions of some sort. It becomes a matter of some importance to observe not only whether the principal products can be accounted for in terms of reactions that are inherently probable, but also

to find some reasonable way to account for the termination of the reaction chains.

On collision with methyl iodide, methyls can capture another methyl, an iodomethyl, a hydrogen atom or an iodine atom as shown by the equations



Probably all of these reactions proceed with an energy of activation around 16 kcal, with the exception of (4) which, because of its endothermic character, will require a greater activation energy. Reaction (5) should be favored over (3) on steric grounds in the ratio of 3 to 1 approximately, which is roughly the proportions of the stable products, CH_4 and C_2H_6 . If hydrogen atoms are formed at all, they would probably yield molecular hydrogen in a combination on the walls. The iodine atoms for the most part end up as sodium iodide and the iodomethyls may either lose iodine at the surface of the sodium (the reaction going more easily than the original iodide-sodium reaction) or may unite to form ethylene and molecular iodine. If the CH_2I loses iodine at the sodium surface, the CH_2 's apparently react there



The carbon is almost certainly formed on the surface for, at the conclusion of the reactions, it is found intimately mixed with the sodium. The reacting vapors never appeared smoky as they would if the carbon was formed in the gas phase. Usually carbon is formed only at rather high temperatures and as a result of slow reactions; its appearance at such low temperatures is uncommon. Several investigators, however, have mentioned in passing the appearance of carbon from reactions of iodide near these temperatures¹² without discussing the manner of its formation.

Ordinarily methylene does not react to give free carbon¹³ but at higher temperatures such reactions may be important, as in the decomposition of ketene at 530° as suggested by Williamson.¹⁴ The general scheme proposed for the

(10) W. H. Carothers and D. D. Coffman, *THIS JOURNAL*, **52**, 1254 (1930); *ibid.*, **51**, 588 (1929).

(11) Disproportionation probably requires a higher energy of activation than combination, cf. C. E. H. Bawn, *Trans. Faraday Soc.*, **35**, 898 (1939); and J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, **6**, 325 (1938).

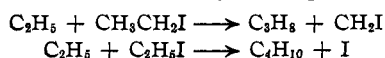
(12) Horn, Polanyi and Style, *Trans. Faraday Soc.*, **30**, 189 (1934); E. W. R. Steacie and R. D. McDonald, *Can. J. Res.*, **10**, 591 (1934); H. P. Meissner and H. J. Schumacher, *Z. physik. Chem.*, **A185**, 435 (1940).

(13) W. F. Ross and G. B. Kistiakowsky, *THIS JOURNAL*, **56**, 1112 (1934); Burton, Davis, Gordon and Taylor, *ibid.*, **63**, 1956 (1941).

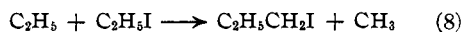
(14) A. T. Williamson, *ibid.*, **56**, 2216 (1934).

reaction accounts for all the observed products by means of reasonable intermediate reactions.

Ethyl Iodide and Mixed Halides.—The possibilities in the ethyl iodide reaction are much more numerous than with methyl iodide alone. The ethyl radical on colliding with ethyl iodide may combine with hydrogen (from either of the two carbon atoms in ethyl iodide), with iodine, methyl, iodomethyl, iodoethyl, or ethyl groups. None of these reactions can be eliminated as completely impossible. The formation of propane and butane is indicated by the equations

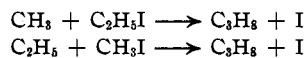


These reactions are expected to be about equally probable. Unsaturated products, including carbon, arise as before from CH_2I . The appearance of a little methane in the gases collected from the ethyl iodide reaction means either that the C-C chain is broken in the original reaction or, what is more likely, in a subsequent reaction of the type shown in equation (8) below.



That the propane is not formed by union of methyl and ethyl radicals is shown by the experiments with the mixed halides where the greatly increased concentration of methyls does not result in any appreciable increase in propane. That the propane production is not diminished by addition of methyl iodide to ethyl iodide means that methyls can enter into some propane-producing reaction with ethyl iodide, and ethyls can enter into a propane-producing reaction with

methyl iodide, the most obvious suggestions being



There is no evidence for the union of either like or unlike alkyl radicals under the conditions of our experiments and it is possible in certain other reaction systems where saturated hydrocarbons have been attributed to this kind of process, that alternative sources are responsible.

Acknowledgment.—The authors express their thanks to Dr. Milton Burton for helpful discussion of many aspects of the work reported in this paper.

Conclusions and Summary

On the basis of a free radical mechanism, one would expect a gas phase Wurtz reaction to be very complicated, and this is found to be true experimentally. The reaction of methyl iodide or ethyl iodide or a mixture of the two at a pressure of about 200 mm. at 320° produces hydrogen, free carbon, saturated and unsaturated hydrocarbons and possibly smaller amounts of higher halides. The character of the products is in harmony with current views concerning free radical reactions.

Combinations of two alkyl radicals to give saturated molecules seem not to occur in this system. Most of the primarily formed free radicals disappear by reaction with excess halide molecules, and the secondary radicals containing iodine disappear either by reacting with each other or by reaction with sodium.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Alkylation of α -Naphthoquinones with Esters of Tetravalent Lead

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This investigation originated in a chance observation made by one of us in attempting to improve a known procedure^{2,3} for converting butadiene-toluquinone (I) into 2-methyl-1,4-naphthoquinone. Treatment of the isomerization product II with silver oxide affords the highly sensitive quinone III, and powerful oxidizing agents lead to some destruction. With chromic anhydride,

(1) On leave of absence from the Department of Chemistry, Lingnan University, Canton, China.

(2) Fieser, Tishler and Wendler, THIS JOURNAL, **62**, 2861 (1940).

(3) Tishler, Fieser and Wendler, *ibid.*, **62**, 2866 (1940).

as in comparable cases,⁴ II can be converted into IV in about 50% yield.

The use of lead tetraacetate was thought to offer a possibility for improvement, for the intermediate quinone III might undergo acetoxylation in one of the activated methylene groups or give a glycol diacetate by an addition to the double bond, and either intermediate should lose acetic acid readily with the formation of IV. When the hydroquinone II was warmed on the steam-bath

(4) Fieser, Campbell and Fry, *ibid.*, **61**, 2206 (1939).