[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Pyrolysis of Amylsodium and the Dissociation of Organoalkali Metal Reagents to Radicals[1]

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This study of pyrolysis of amylsodium and pentenylsodium shows that the process is more complicated than is commonly supposed. Pentane and pentene are obtained from the former but these gases may very well arise from consecutive reactions rather than as primary products. The interpretation as a dissociation to two radicals is discussed and the general feasibility of this concept for interpreting the chemical behavior of organoalkali metal reagents is considered.

This paper presents data which show that at least two consecutive reactions complicate tracing the primary course of pyrolysis and may conceal the path altogether. Also recent objections by Bryce-Smith[2] to the idea that organoalkali metal reagents can produce radicals are ascribed to a failure to consider the important role of atomic sodium, derived from such a dissociation. A further clarification of the biradical concept is presented.

The pyrolysis experiments extend the previous work[2] in which *trans*-pentene-2 was obtained, surprisingly, instead of pentene-1. The pentane and pentene balances for decompositions at 75° and 90° are shown in Table I together with the present results at 100°. In no case did all of the hydrocarbon moiety escape from the aggregate, although the amount increased as the temperature rose, as would be expected. At 50° decomposition was extremely slow and collection of gas was stopped arbitrarily.

At least two consecutive reactions obscure the initial step. The first is the metalation of pentene by amylsodium. The second is the decomposition of pentenylsodium, the product of metalation. The formation of *trans*-pentene-2, which was given the principal attention in the previous paper[3] may be an additional reaction in case metalation is not a prerequisite for isomerization.

Metalation as per equation (1) yields pentane.

$$C_5\overset{-}{H}_{11}\overset{+}{Na} + C_5H_{10} \longrightarrow C_5H_{12} + \overset{+}{Na}[\overset{-}{C}H_2 \mathrel{\overset{\cdots}{-}} CH \mathrel{\overset{\cdots}{-}} CHC_2H_5] \qquad (1)$$

The amount produced, even in the first 10% of reaction (see Table I) is high enough to leave little doubt of the large amount of this reaction.

TABLE I

Pentane and Pentenes at Maximum and Partial (10%) Decomposition of Amyl- and Pentenyl-Sodium

R[a] of RNa	Temp., °C.	Time, hrs.	Maximum Decomposition[b]				10% Decomposition[c]		
			%	RH	P-1	P-2	RH	P-1	P-2
Am	50	48	21[d]	82	0	18	86	0	14
Am.	75	21	67	29	20	51	52	17	31
Am.	90	8.3	81	43	37	20	68	15	17
Am.	100	5.3	88	47	28	25	48	23	29
Pen.	100	5.0	71	0	5	95	0	5	95

[a] Am. and Pen. signify amyl and pentenyl respectively. [b] The amounts of different hydrocarbons by the end of the decomposition are estimated by appropriate graphing of the data in Table I of the previous paper[3] and Table II of this paper. Maximum decomposition signifies that no appreciable liquid condensate was caught in the liquid nitrogen trap within 30 minutes. P-1 signifies pentene-1, P-2 refers to *trans*-pentene-2. [c] These values are estimated by extrapolations and other comparisons from appropriate graphs of pentane and pentene at increasing amounts of decomposition. [d] This decomposition was not carried to the maximum amount but the total decomposition would not have exceeded 42% and was probably less.

In turn, the product of metalation, pentenylsodium, decomposes, as shown in Table I. The later stages of pyrolysis should accordingly be high in pentene. The decomposition is relatively easy, however, and some of the pentene in the early stages probably comes in this way.

A lower temperature does not eliminate these secondary steps. The very high proportion of pentane in the first 21% of decomposition at 50° is clear evidence for a large amount of metalation. The presence of *trans*-pentene-2 as the only olefin cannot be reconciled as a product of the initial step.

For all these reasons no assurance can be given that any of the gases collected represent a primary step. Such a rapid sequence of reactions is typical of many processes which occur with these highly

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(1) This work was performed as a part of the research project sponsored by the National Science Foundation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

(3) Morton and Lanpher, *J. Org. Chem.*, **20**, 839 (1955).

reactive reagents. An earlier paper[4] has labeled such changes as "cascading reactions."

The initial phase of pyrolysis is assumed to be a dissociation to two radicals, as in equation (2).

$$C_5\overset{-}{H}_{11}\overset{+}{Na} \longrightarrow C_5H_{11}\cdot + Na\cdot \qquad (2)$$

These radicals may disproportionate with each other to give the thermally more stable sodium hydride and pentene, as in equation (3). The pentene

$$Na\cdot + \cdot C_5H_{11} \longrightarrow NaH + C_5H_{10} \qquad (3)$$

would be metalated promptly by amylsodium, as in equation (1). If conditions permitted the agglomeration or removal of sodium metal, the pentyl radical would dissociate with itself to give pentene and pentane. The amount of this change could not possibly be large because of the tendency of atomic sodium to form a new and more stable salt whenever possible. The emphasis given in a previous paper[5] to the easy decomposition of amylsodium was not intended to imply an absence of (a) a metalation, equation (1), which has long been a common reaction in this laboratory or (b) a change to a more stable salt as in equation (3). At best only a small fraction of amylsodium can revert completely to metallic sodium. This amount was not measured in the previous work[5,6] and later experiments[7] indicate that it is less than may have been implied. A large amount of sodium hydride is formed as would be expected. The whole problem has been under experimental review for some time as the previous paper[3] and the present one indicate. More work[7] will be published later. The problem has proved more complicated than was expected.

Bryce-Smith[2] has taken exception to the idea of radicals from this class of reagents on the grounds (a) that butyllithium dissociates to butylene and lithium hydride; (b) that the formation of radicals from such a source seems out of line with other methods, such as the pyrolysis of tetraethyl lead and (c) that a test for alkyl radicals with isopropylbenzene failed to show any 2,3-dimethyl-2,3-diphenylbutane.

The claim for a primary dissociation of butyllithium to lithium hydride and butene—actually he obtained 60% butene and 40% butane in the total product—is without significance in the light of the present results. These proportions are within the ranges obtained with amylsodium. But even if all of the hydrocarbon product were the alkene, the formation as per equation (3) would be consistent with the assumption of biradicals.

The second and third points are also without significance because no concern was given to the reactivity of the sodium radical. Attention has previously been called to the effect which atomic sodium should have in Wurtz disproportionation[5] and in metalation.[8,9] The discussion of Bryce-Smith is based on the assumption that the metal radical can be neglected and the alkyl radical only be considered. A brief elaboration of the biradical concept should help to remove this erroneous view and to clarify the new idea.

The literature shows that the assumption of homolytic dissociation for many alkali metal salts is, after all, very reasonable. Pauling[10] has discussed the case of sodium chloride. As the bond distance between the ions increases the energy curves for heteropolar and homopolar states intersect. Thermal dissociation should produce radicals. Cesium fluoride is different. Its curves do not intersect. Dissociation should produce ions. But Pauling explained this difference on the grounds that the electron affinity of fluorine (98 K.cal/mole) exceeds the ionization potential of cesium (89 K.cal/-mole). The reverse is true for sodium chloride, where the respective values are 92.5 and 117.9 K.cal/mole. For the majority of the halide salts, these values are in the same order as for sodium chloride.

The electron affinity for carbon varies but one value is around 31[11] which is well below the ionization potential for sodium. Also Baughan, Evans, and Polanyi[12] calculated that the respective curves for methylsodium intersect. Therefore bond stretching, which is usually regarded as occurring during chemical changes should lead easily to a biradical transition state. Heat is one way to induce stretching. Association with certain polar salts in an ionic aggregate probably is another way. Coordination[9,13] of an organic compound about the cation should also distend the bond. Coordination requires unshared electrons in the organic compound. The importance of this electrophilic step by the sodium reagent is implied by the fact that to date no reaction of amylsodium with an organic compound has been possible unless such electrons are present.[13]

Attention can next be given to the reactions which might be expected from the two radicals which are produced in equation (2). Atomic alkali metal should lose an electron easily and become a cation again in a more stable salt where the anion component would usually, but not necessarily, be from a stronger acid. Carbon has, on the contrary, no greatly one-sided and corresponding activity. Therefore the atomic metal should set the course

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[4] Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950).

[5] Morton and Cluff, *J. Am. Chem. Soc.*, **74**, 4056 (1952).

[6] Morton and Cluff, *J. Am. Chem. Soc.*, **75**, 134 (1953).

[7] Morton and Ward, Research in progress.

[8] Claff and Morton, *J. Org. Chem.*, **20**, 981 (1955).

[9] Morton, Claff and Collins, *J. Org. Chem.*, **20**, 428 (1955).

[10] Pauling, *Nature of the Chemical Bond*, 2nd Ed., Cornell University Press, 1944, pg. 44, 66.

[11] Remick, *Electronic Interpretations of Organic Reactions*, 2nd Ed., John Wiley and Sons, Inc., N. Y., 1949, pg. 122.

[12] Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

[13] Morton and Brachman, *J. Am. Chem. Soc.*, **76**, 2980 (1954).

of chemical change, and one should look first for a reaction which produces a new salt rather than expect reactions that are typical for alkyl radicals which are produced under other circumstances, say from the decomposition of lead tetraethyl. The use of isopropylbenzene as a detector for alkyl activity would usually be fruitless. Lithium hydride and butylene should predominate. 2,3-Diphenyl-2,3-dimethylbutane should form only in minute amounts and possibly not at all.

The original reason for suggesting that these sodium reagents dissociate to two radicals came from the work on Alfin polymerization of butadiene. The structure of the polymer was chiefly 1,4-, almost the same[14] as was found in products prepared by free radical reagents and quite unlike that derived from ordinary sodium compounds. The idea received some support from the study[5,6] of pyrolysis. The calculation of energies in disproportionation,[5] the cleavage of ether,[15] the metalation of hydrocarbons,[8,9] and the comparative activities of lithium, sodium, and potassium reagents all had a more probable explanation on the biradical basis than by the anionic one.

Many chemists may have felt that this new idea violated an accepted principle that all alkali metal reagents could be judged as anionic. Actually the old concept is an extrapolation from the behavior in dissociating solvents where ions are separated and can act independently. For the more active organosodium reagents, however, no conditions more adverse for dissociation as ions could be found. The medium is a saturated hydrocarbon and the reagent is insoluble. That is to say, the association is at a maximum and dissociation as ions is at the minimum. Yet these reagents are among the most active in organic chemistry.

The persistence of the anionic concept in the face of conditions so very unfavorable for anion activity is caused possibly by an understandable prejudgment that a reaction which begins with a salt and ends with another salt must remain as a salt or ion at all intermediate points. That deduction is no more warranted, however, than the assumption that a traveler leaving a hotel by taxicab in one city and arriving at a hotel by taxicab at a distant city has travelled the intervening miles by taxicab. Even when other circumstantial evidence—cabs of like make and color or drivers with similar build and apparel—can be cited, such a deduction would not be drawn. Yet the corresponding opinion has been given great weight in these reactions. Once this presumption of an anionic mandate is removed, the way is open to a fair consideration of the facts.

The concept of dissociation to two radicals is, after all, very simple and orthodox. Naturally there will be cases where either the radical pair, the ion-pair, or the anionic concept may seem equally suitable. For such cases the long-standing rule[16] in science has been that the concept which can be applied to the most facts with the least amount of modification is preferred for general use. The radical pair theory fits this situation nicely, and makes possible a common basis for the interpretation of most cases.

The concept does not say that the reagents never act as ion pairs, as suggested at an early stage in the development of the present ideas[13,17,18] or even as anions only. On the contrary, it admits the great reactivity that can exist in those forms if the environment is made favorable for them, or if the carbanion is stable enough to exist as such, or if the reaction is of suitable type. Perhaps the last is true for the ion interchanges which occur with halide salts[6] or alkoxides[8] in an ionic aggregate.

A proper classification of these highly versatile reagents merits attention. With fairness they might be called electrophilic[17,18] because the first step with most organic compounds can be assumed to be coordination. Indeed the idea of complexing with organic compounds seems well suited to explain the anomaly that chlorobenzene is more reactive with amylsodium and with o-sodioanisole[13] than is amyl chloride. Moreover the electrophilic influence seems to outweigh the nucleophilic one, even in an ion-pair reaction. A designation as nucleophilic or anionic or strongly basic would appear to be incorrect. Neither the anion nor the radical from the anion seems to have a role important enough to justify naming the whole by a minor part. The ex-

TABLE II

PYROLYSIS OF AMYL- AND PENTENYL-SODIUM AT 100°

R of RNa	Fract. No.	Time, hrs.	Yield, mg.	Pentane, %	Pentene -1 %	Pentene -2 %
Am.	1	0.3	872	53	24	23
	2	0.6	1661	58	27	15
	3	1.0	567	50	32	18
	4	1.3	297	28	37	35
	5	2.3	326	14	33	53
	6	5.3	64	10	11	79
			3787[a]			
Pen.	1	0.3	694	0	5	95
	2	0.6	447	0	5	95
	3	1.0	250	0	5	95
	4	2.0	422	0	5	95
	5	5.0	150	0	5	95
			1963[b]			

[a] This quantity equals 52.5 m.e. of C_5 hydrocarbons from an original sample of 60.5 m.e. [b] This quantity equals 28.1 m.e. of C_5 hydrocarbons from an original sample of 39.4 m.e.

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(14) Morton, Nelidow and Schoenberg, *Preprint, Third Rubber Technology Conference*, The Institution of the Rubber Industry, London, June, 1954.

(15) Morton and Brachman, *J. Am. Chem. Soc.*, **76**, 2973 (1954).

(16) Russel, *A History of Western Philosophy*, Geo. Allen and Unwin, Ltd., 1948.

(17) Morton, *Chem. Revs.*, **35**, 1 (1944).

(18) Morton, *J. Am. Chem. Soc.*, **69**, 969 (1947).

pression "reactive salts" is preferred because both components are needed for the succession of steps which occur in a reaction. Another advantage is that no mechanism is implied. The reagent can function either as a radical or ion pair depending upon the environment or reaction concerned.

EXPERIMENTS

The general procedure for amylsodium was described in the previous paper.[3] The first four or five fractions were collected at 20-minute intervals. The reason for the large quantity in the second fraction is not clear but the same result was found in the decomposition at 90°, recorded in the previous paper. The results are recorded in Table II.

Pentenylsodium was prepared by metalation of pentene-1 by amylsodium. The mixture had stood for three months before it was pyrolyzed. The hydrocarbons were analyzed by infrared analysis as in the case of amylsodium.

The residues from both reactions were carbonated by adding the solid particles to solid carbon dioxide. Both solids became hot and the one from pentenylsodium became almost incandescent. Eventually the solids were ground in a mortar with solid carbon dioxide. Water was added and the aqueous solutions were acidified and extracted successively by pentane, ether, and *tert*-butyl alcohol. Tarry acids predominated and known compounds were not obtained by this method.

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