[CONTRIBUTION NO. 8 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND CO.]

THE THERMAL DECOMPOSITION OF SODIUM ETHYL

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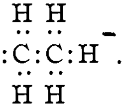
Application of the octet theory to sodium ethyl leads to the completely polar formula Na^+  $:\overset{H}{\underset{H}{C}}:\overset{H}{\underset{H}{C}}:H^{-}$. A non-polar or partially polar formula is excluded by the fact that each of these ions has a complete octet. Sharing of electrons between them is therefore impossible.

Sodium alkyls have been prepared in a state of approximate purity by Schlenk and Holtz[1] and their physical properties may be compared with those listed by Lewis[2] as typical of polar substances. They are non-volatile solids which do not melt without decomposition. They are insoluble in petroleum ether and benzene. That they are capable of behaving as true electrolytes has been established by the important work of Hein.[3] Hein showed that solutions of sodium ethyl in zinc ethyl conduct (zinc ethyl is a non-conductor); that the conduction follows Faraday's law; that the ethyl group is actually involved as an anion in the transport of the current; and that it is discharged at the anode with the formation of ethylene and ethane.[4]

The theory and the facts thus agree in all particulars and it seems completely justified to assume that sodium ethyl is composed of sodium ion and ethyl anion. This latter represents one of the possible reactive species of ethyl, and indeed the only one which is capable in a certain sense of being isolated. The spontaneous changes which it undergoes are therefore of considerable theoretical interest. Moreover, these spontaneous changes occur smoothly at temperatures well below 100°, a fact which provides some assurance of the absence of deep-seated secondary reactions.

Wanklyn, who in 1858 prepared $Zn(C_2H_5)_2 \cdot NaC_2H_5$, the earliest known example of a sodium alkyl, observed that it was decomposed by rather gentle heating with the formation of gases and a residue consisting of a mixture of sodium and zinc. Of this behavior he says,[5] "this reduction of a sodium compound by mere heating is, I think, unique, and is to be regarded as a chemical anomaly."

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[1] Schlenk and Holtz, *Ber.*, **50**, 262 (1927).

[2] Lewis, THIS JOURNAL, **38**, 763 (1916).

[3] Hein, Petzschner, Wagler and Segitz, *Z. anorg. allgem. Chem.*, **141**, 161 (1924).

[4] When a lead anode was used the product was lead tetra-ethyl.

[5] Wanklyn, *Ann.*, **108**, 67 (1858).

The thermal decomposition of sodium ethyl was studied by Schorigin,[6] who observed that the gaseous products consisted exclusively of ethylene and ethane in equivalent amounts. This is, of course, a result which might be expected if the ethyl anion were to lose one electron to the sodium cation with the formation of the ethyl radical. The peculiarity of Schorigin's results which led to a repetition and extension of his experiments was the fact that the first fractions of the gas contained more ethane than ethylene and the last more ethylene than ethane. Such behavior is inconsistent with the assumption that the first products of the reaction are metallic sodium and the ethyl radical.

Schorigin carried out his experiments by mixing mercury ethyl and sodium wire in an atmosphere of nitrogen and immediately heating the mixture until thermal decomposition set in and was complete, the gas being collected over water containing sodium hydroxide and saturated with sodium chloride. The last portion of the hydrocarbon gases was swept into the receiver by a stream of carbon dioxide. In preliminary experiments made by the writers in this way the gas obtained was found to consist chiefly of ethylene. A similar result was obtained when the compound $Zn(C_2H_5)_2 \cdot NaC_2H_5$ was prepared in the pure state and decomposed *in vacuo,* and when sodium ethyl prepared by the method of Schlenk and Holtz was isolated and decomposed *in vacuo.*

All of these methods involved experimental difficulties capable of introducing large errors, and all of the data here presented were obtained by the following procedure.

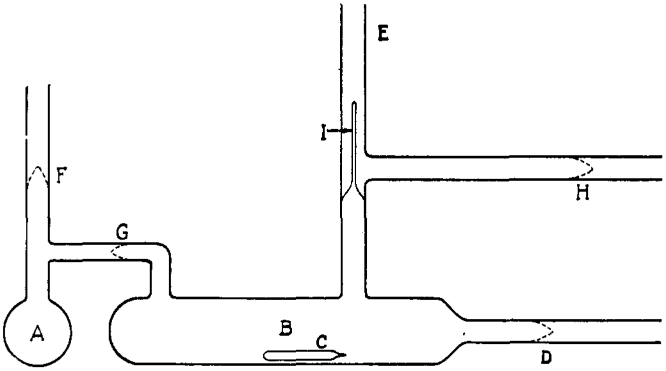

Fig. 1.

Preparation of the Sodium Ethyl.—The tube B containing a known amount of mercury ethyl in the sealed capsule C was sealed at D to a high vacuum line. A large excess of sodium (1–2 g. in all) was placed in the flask A, which was then sealed off at F. The mercury vapor pump was then started and when the pressure had been reduced to less than 0.1 micron, the sodium was distilled into the tube B by heating A with a

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[6] Schorigin, *Ber.*, **43**, 1931 (1910).

free flame, the tube C being cooled by a stream of water falling on B. The sodium condensed as a bright mirror completely covering the walls of B. After the distillation the flask A was removed by sealing at G and the tube B was sealed off at D. The tube B was then shaken vigorously to break the capsule C. The thinner portions of the sodium mirror were rapidly blackened by the mercury ethyl: after standing for twelve hours the liquid in the tube had completely disappeared and black granules were present which could readily be broken loose from the surface. After a period of twenty-four to forty-eight hours no trace of mercury ethyl could be found in the tube. These results indicated that mercury ethyl is, under these conditions, quantitatively converted into sodium ethyl.

To obtain the products of the thermal decomposition of the sodium ethyl, the tube B was sealed at E to a Toepler pump and an iron slug was placed in H, which was then sealed. After the system had been completely evacuated, the iron slug was raised by a magnet and allowed to fall on the valve I, thus opening the tube B to the system. The tube B was placed in an oil-bath. The gas was pumped off as it was evolved and collected over mercury.

Analysis of Gases.—The precise analysis of small samples of hydrocarbon gases presents experimental difficulties which have not yet been completely solved. It is thought, however, that none of the analytical results here presented is sufficiently in error to affect any of the conclusions of this study. The apparatus used was that of Bone and Wheeler,[7] which permits the use of 5–20 cc. samples. Hydrogen was determined by direct absorption with Paals' Pd-sol. Ethylene was absorbed by bromine water containing potassium bromide. This reagent slowly attacks ethane also, so that there is some uncertainty in the ethylene : ethane ratios.

Experimental Results

Experiment 7.—Sodium ethyl from 1.312 g. of $Hg(C_2H_5)_2$ and 1.5 g. of sodium was decomposed. Between room temperature and 142°, 213 cc. of gas (S. T. P.) or 94% of the calculated amount was obtained. Of this gas, 6 cc. was present before heating; 7.5 cc. was evolved between 29 and 90° and about 14.5 cc. between 117 and 142°.

Anal. C_2H_4, 84.30; H_2, 0.24; C_2H_6 (by contraction), 14.95; C_2H_6 (by absorption), 14.97; total, 99.51; *C/A*, 1.248; C_2H_4/C_2H_6, 5.63.

$$C/A = \frac{\text{Contraction in volume due to combustion}}{\text{Contraction in volume due to absorption by KOH}} = \frac{H_2O}{CO_2}$$

Calcd. for ethane, 1.250.

At 142° pumping was continued until no more gas was evolved. The oil-bath was then removed and the tube heated with a free flame. Gas was again copiously evolved. In all 107.5 cc. of gas (S. T. P.) was collected. This gas proved to be nearly pure hydrogen.

Anal. (1) C_2H_4 (by Br absorption) 1.11; H_2 (by Pd absorption) 97.65; C_2H_6 (by difference) 1.24; C_2H_4 (by Br absorption) 1.24. (2) By combustion and absorption, H_2, 97.70; C_2H_6, 1.22.

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[7] See Grice and Paymen, *Fuel Science Practice*, July, 1924.

Although the *C/A* ratio indicated the absence of higher hydrocarbons, a special search for butane was made as follows: 150 cc. of the gas of Experiment 7 was placed in communication with an evacuated bulb of 10 cc. capacity which was immersed in a mixture of carbon dioxide snow and acetone. No liquid was observed to condense. The bulb while still in the freezing mixture was sealed off and after warming was opened under mercury so as to transfer the gas directly to the gas analysis apparatus. Some air was admitted during this process. Ethane found by contraction was 11.52 and by absorption 11.80%, the ratio being 1.218. Assuming no experimental error in the analysis, this would indicate the presence of about 0.03% of butane in the original sample.

Experiment 8.—The following experiment is typical of those in which the gas was collected in a series of fractions and each fraction analyzed separately: 0.635 g. of mercury ethyl; 1.0 g. of sodium.

Frac.	Temp. of bath, °C.	Vol. of gas, cc.	C_2H_4	C_2H_6 By contr.	C_2H_6 By abs.	Total	*C/A*	$\frac{C_2H_4}{C_2H_6}$
1[a]	20	3	26.87	69.50	67.50	94.37	1.29	0.41
2	90	26.0	74.10	24.98	25.50	99.60	1.225	2.91
3	90	16.2	85.70	13.90	13.71	99.41	1.267	6.25
4	90	18.5	88.20	11.30	11.24	99.64	1.257	7.85
5	91	16.4	89.60	9.78	9.80	99.40	1.247	9.14
6	90	20.0	89.40	10.03	10.05	99.40	1.248	8.90
7	90–150	8.9	86.85	12.17	11.62	99.43	1.312[b]	7.48

Total, 109.0 cc. = 102.6 cc. (S. T. P.) or 94% of calcd. amount.

[a] Large experimental error owing to small volume of gas.

[b] Including 0.96% of H_2.

Discussion of Results

The analytical data indicate the presence of not more than traces of any other substances than ethylene and ethane in the gases evolved below 150°. Repeated qualitative tests for acetylene were negative and the data of Expt. 7 indicate the absence of higher hydrocarbons.

The data of Expt. 7 show that the gas formed between 25 and 142° consists of ethylene and ethane in the ratio 5.6:1 and that after the reaction has completely stopped at 142°, large amounts of hydrogen are evolved on heating to much higher temperatures. The only obvious way of accounting for this is to suppose that the principal reaction is the transformation of sodium ethyl into ethylene and sodium hydride. The sodium hydride then decomposes at higher temperatures with the liberation of hydrogen.

$$NaC_2H_5 \longrightarrow NaH + C_2H_4 \qquad (1)$$

$$2\,NaH \longrightarrow 2\,Na + H_2$$

Using the polar formula given above, this reaction involves simply the elimination of the unshared electron pair of the ethyl anion together with one of the protons as hydride ion.

In this connection it is interesting to observe that Jolibois[8] found that both $Mg(C_2H_5)_2$ and C_2H_5MgI decompose at 175° with the formation of ethylene, leaving a residue of MgH_2.[9]

To account for the presence of ethane, one may suppose that the following reaction occurs

$$2\ NaC_2H_5 \longrightarrow Na_2C_2H_4 + C_2H_6$$

This reaction involves simply the transfer of a proton from one ethyl anion to another. The first ion thus becomes a doubly charged anion and the second the neutral molecule, ethane. If one regards ethane as a very weak polybasic acid, this reaction finds many analogies. Thus, $NaOHCH_2CH_2OH$ on heating is converted into $NaOCH_2CH_2ONa$ and $HOCH_2CH_2OH$.

The data of Expt. 8 show that the gas which is slowly formed at ordinary temperature contains more ethane than ethylene,[10] and there appears to be no simple and obvious way to account for this other than by the equation represented above.

Some idea of the fate of the $Na_2C_2H_4$ may be obtained from a study of the data in Expt. 7. These data show

Sodium ethyl used = 0.01015 mole
H_2 found 105 cc. = 0.00469 mole
C_2H_4 found 180 cc. = 0.00804 mole
C_2H_6 found 33 cc. = 0.00147 mole
Deficit = 0.00064 mole

The number of atoms of hydrogen thus considerably exceeds the number of moles of ethylene, and the total ethane and ethylene lacks 6% of accounting for all of the sodium ethyl. These facts may be accounted for by assuming the following changes

$$\begin{array}{ll}
4\ NaC_2H_5 & \longrightarrow 2\ Na_2C_2H_4 + 2\ C_2H_6 \\
2\ Na_2C_2H_4 & \longrightarrow C_2H_6 + Na_2CHCHNa_2 \\
Na_2CHCHNa_2 & \longrightarrow 2\ NaH + NaCCNa \\
\hline
4\ NaC_2H_5 & \longrightarrow 3\ C_2H_6 + H_2 + 2\ Na + NaCCNa
\end{array}$$

In this series of reactions, which resulted in the formation of 0.00147 mole of ethane, there would be formed 0.00049 mole of sodium acetylide while the carbon deficit would require 0.00064 mole. Unfortunately, no test on the residue for sodium acetylide was made. It was, however, observed, after no more gas was produced by strongly heating the residue, that the admission of air to it caused a brilliant flash of fire. Corresponding to the ethane, there would also be formed 0.00049 mole of hydrogen. When this is subtracted from the 0.00469 mole of hydrogen found, one obtains 0.00420 mole, whereas the 0.00804 mole of ethylene found would require, in accordance with Equation 1, 0.00402 mole. The agreement is all that could be expected from data of this type.

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[8] Jolibois, *Compt. rend.*, **155**, 353 (1912).

[9] Jolibois makes no mention of the presence of any ethane in this gas.

[10] This has been repeatedly verified in other experiments not reported here.

The precise verification of these relationships must await more elaborate experiments, which cannot be performed at this time.

The manner in which the ethylene : ethane ratios changed from less than 1 to more than 9 in successive fractions and then fell off again toward the end clearly indicates the presence of a series of successive reactions or of simultaneous reactions with different temperature coefficients.

One simple and quite obvious reaction finds no place in the above scheme

$$NaC_2H_5 \longrightarrow Na + C_2H_5—$$

In this reaction the ethyl anion loses one of its unshared electrons to the sodium ion and is converted into the ethyl radical which may then undergo disproportionation or polymerization. It seems possible that the ethyl anion may, under certain conditions, behave in this way (*cf.* the work of Hein referred to above), and, assuming the correctness of Schorigin's results, this reaction might completely describe the thermal decomposition of sodium ethyl. This reaction requires, however, that ethane and ethylene be formed in precisely equivalent amounts. In all experiments made by the writers with sodium ethyl prepared by various methods, the ethane constituted only a relatively small fraction of the gas evolved and the nature of the data indicates that only a small part of it could have been formed by this reaction.

Summary

1. Mercury ethyl reacts completely with an excess of sodium *in vacuo* with the formation of sodium ethyl.

2. The thermal decomposition of sodium ethyl (in the presence of sodium and mercury) begins very slowly at room temperature and is quite rapid at 100°.

3. The gas formed by the thermal decomposition of sodium ethyl at temperatures in the neighborhood of 90–100° consists of ethylene and ethane in the ratio of about 85 to 15. Sodium hydride is found in the residue. The principal reaction is, therefore, $NaC_2H_5 \longrightarrow NaH + C_2H_4$.

4. The gas formed by the spontaneous decomposition of sodium ethyl at ordinary temperature contains more ethane than ethylene. This is supposed to be due to the reaction $2NaC_2H_5 \longrightarrow Na_2C_2H_4 + C_2H_6$. The analytical data furnish some information concerning the fate of the $Na_2C_2H_4$.

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