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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXIII. The Effect of Alkali Metal Halides upon Amylsodium[1]

BY AVERY A. MORTON AND EDWARD F. CLUFF

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A previous paper[2] has shown that tertiary pentoxides which accelerate the reactions of amylsodium also accelerate the thermal dissociation of that reagent into radicals. The present paper describes the influence of alkali metal halides upon the stability of amylsodium. This study is important because amylsodium, as prepared from amyl chloride and sodium, contains a little more than an equal molal quantity of sodium chloride and probably derives some activity from association with that supposedly inert salt in view of evidence[3] that an alkali metal halide is essential for Alfin catalysis. The present work shows that these salts do indeed affect the decomposition of amylsodium and in proportion to the relative sizes of the component ions.

Commercial halide salts were used because some of the alkali metal fluorides are difficult to prepare in a Wurtz reaction, and because positive effects could be obtained with granular salts in spite of the fact that they are incorporated[3] in the aggregate with difficulty. Each dried salt was added to about a mole equivalent of amylsodium–sodium chloride, which had been prepared by the standard method[4] from amyl chloride and sodium at −10° and was ground in the high-speed stirring apparatus[5] at a specified r.p.m. for 1.5 hours. The mixture was next heated—usually to 50° for three hours—and was then carbonated on solid carbon dioxide in order to convert all organosodium compounds to sodium carboxylates. The caproic acid therefrom represented amylsodium. The water-soluble carboxylic acids, as explained in the earlier paper,[2] came from a dimetalation of pentene which in turn had come either from a small amount of disproportionation during the preparation of amylsodium or, if in large amount, from pyrolysis of amylsodium. Decane also formed in about 7% yield during the preparation of amylsodium but in excess of that amount was a consequence of pyrolysis. Some higher boiling material proved to be a mixture of diamyl ketone, triamylcarbinol and a hexadecene. These products were formed only when lithium bromide was used and were therefore nicely accounted for by the assumption that ion interchange took place—equation 1—and that during carbonation the lithium caproate

$$C_5H_{11}Na + LiBr \longrightarrow C_5H_{11}Li + NaBr \qquad (1)$$

as lithium salts may do,[6] acted in a cascade of reactions, equation 2, to give the ketone and tertiary carbinol. Dehydration

$$C_5H_{11}Li + CO_2 \xrightarrow{(1)} C_5H_{11}CO_2Li \xrightarrow{(2)} (C_5H_{11})_2CO \xrightarrow{(3)} (C_5H_{11})_3COLi \qquad (2)$$

of the latter during distillation would give a hexadecene.

All results are listed in Table I. The first three experiments are controls to establish the range of yields of amylsodium without pyrolysis. That they are a little higher than the 80% reported[5] earlier can be credited to small improvements in the technique and probably more to the better grade of amyl chloride[7] regularly used. The next two show the yields after three hours at 50° with no halide salt added. Experiments 6–14, inclusive, are arranged primarily in the order of decreasing amount of amylsodium, as represented by caproic acid, and, secondarily, in increasing amount of water-soluble acids, but all changes are small and for decane are nil.

Decisive effects are evident in experiments 15–19 where sodium iodide and lithium bromide were used. Sodium iodide caused a small drop in amylsodium in no. 15 and a sizable one in no. 16, accompanied by a considerable gain in the water-soluble acid. The next two experiments with the same salt but at higher temperatures were aimed at increasing the percentage of decane—supposedly an unusual product[8] of pyrolysis—and did so to a limited extent in no. 18. Lithium bromide, in no. 19, caused a greater drop in amylsodium than did sodium iodide and was responsible also for the ketone, carbinol and hexadecene mentioned before.

Potassium fluoride in 20–21 acted differently from the preceding salts in that a gain in water-soluble acid took place without a significant loss of amylsodium. Indeed totals of 91 and 94%, respectively, of organosodium compounds based on the amyl chloride originally used were obtained. These quantities were higher than in the controls and suggested that some hidden or less stable amyl-

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[1] The authors are indebted to the Synthetic Rubber Division, Reconstruction Finance Corporation, for financial support of this work.

[2] A. A. Morton and E. F. Cluff, THIS JOURNAL, **74**, 4056 (1952).

[3] A. A. Morton, F. R. Bolton, E. F. Cluff and F. E. Collins, *Ind. Eng. Chem.*, **44**, 2876 (1952).

[4] A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little and R. L. Letsinger, THIS JOURNAL, **72**, 3785 (1950).

[5] A. A. Morton and L. E. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

[6] H. Gilman and P. R. VanEss, THIS JOURNAL, **55**, 1258 (1933).

[7] A. A. Morton and A. E. Brachman, *ibid.*, **73**, 4364 (1951).

[8] J. F. Lane and S. E. Ulrich, *ibid.*, **73**, 5470 (1951).

TABLE I

EFFECT OF ALKALI METAL HALIDES ON THE STABILITY OF AMYLSODIUM

Expt. no.	Halide salt	Temp., °C.	Time, hr.	Cap. acid, %	Water-soluble acids, %	Decane, %	High-boiling cpds.,[a] %
1	Control	−10	0	89	0	3	
2	Control	−10	0	86	0	4	
3	Control	−10	0	84	0	7	
4	None	50	3	81		6	
5	None	50	3	79	4	6	
6	LiCl	50	3	80	4	6	
7	KCl	50	3	80	4	5	
8	NaCl	50	3	78	5		
9	KBr	50	3	78	5	6	
10	KI	50	3	77	7	6	
11	NaBr	50	3	74	5	6	
12	NaSCN	50	3	73	5		
13	LiF	50	3	73	6	4	
14	NaF	50	3	73	10	5	
15	NaI	50	3	71	8		
16	NaI	50	3	52	23	6	
17	NaI	65	7	30	10	7	
18	NaI	80	3	40	10	11	
19	LiBr	50	3	51	8	6	17
20	KF	50	3	78	13	4	
21	KF	50	3	78	16	2	
22	KF	−10	0	94			
23	KF	−10	0	87	3		
24	NaF	−10	0	88			
25	NaF	−10	0	92			
26	LiF–KI	50	3	78	8	5	
27	KF–LiBr	50	3	78	5	5	0
28	KF–LiBr	50	3	51	7	6	20
29	NaI–NaOR[b]	50	3	34	33	12	
30	NaI–LiBr	50	3	35	9	7	26
31	KOR[b]	80	3	12	23	10	

[a] Calculated on the basis that all material is diamyl ketone. [b] R = *t*-pentoxide.

sodium was not revealed by the ordinary carbonation and was stabilized against pyrolysis in some manner by potassium fluoride. Accordingly, experiments that paralleled the controls, but with potassium fluoride present, were carried out (no. 22–23) with the result that 94% of caproic acid was obtained, the highest so far in years of study and hundreds of experiments with this reagent. Sodium fluoride was not the equal of potassium fluoride as a stabilizer. The two experiments (no. 24 and 25), recorded in the table, were the best obtained from a series not recorded here where the yield was usually no better than in the controls. Actually in the four experiments (20 to 23) where potassium fluoride was used the yield of total acid (caproic acid plus water-soluble) never fell below 90%, whereas in all the experiments with sodium fluoride it rose above 90% only once. Sodium fluoride seemed also to be affected considerably by the heat used in drying the salt.

The remaining experiments in the table are with pairs of halide salts, each used in the same quantity as for the test with the single salt. In general the effect on amylsodium was the same as caused by one or the other of the separate salts and, in the majority of cases, followed that of the salt that caused the most decomposition. The lithium bromide–sodium iodide pair, however, proved (no. 30) a notable exception in that the changes exceeded the action of either salt. Such a result should have followed any formation of lithium iodide by ion interchange. The experiment was, in fact, carried out in the hope that such an interchange might occur and increase the loss of amylsodium.

The assumption of ion interchange within the aggregate appears reasonable for a change from amylsodium to amyllithium and also for sodium iodide to lithium iodide, which was more difficult because granular salts were involved. No change to amyllithium took place, however, when lithium fluoride and lithium chloride were used nor did it seem to take place in some of the pairs of salts. A favorable circumstance, therefore, appears to exist when the change leads to the formation of a less reactive organoalkali metal compound and where also the halide ion is large.

The halide salts here tested have in common the sodium chloride cubic crystal type and are uni-univalent. Hence the differences which they cause could come from differences in the relative sizes of cation and anion. For sodium chloride, which is normally associated with amylsodium—because of the manner of preparation—the ratio of the radii of the two ions is 0.53. For sodium iodide (0.44) and lithium bromide (0.31) the ratios are appreciably less and for potassium fluoride (1.0) the ratio is greater. For all other salts of this crystal type, it is near that for sodium chloride. Hence the degree and direction of the effects seem in proportion to the heterogeneity introduced into the ionic aggregate. This view might be extended to the much greater heterogeneity and larger effect caused by alkoxides, since in no case did the effect with a halide salt equal that induced by the tertiary pentoxides. For example, sodium iodide contributed nothing in the presence of sodium *t*-pentoxide (no. 29) and potassium *t*-pentoxide at 80° (no. 31) was far and away more effective than the corresponding experiment (no. 18) with sodium iodide. However cases, such as the Alfin catalyst,[3,9] exist where highly specific effects are attained by specific salts and where heterogeneity alone does not suffice to explain all results.

Experiments

General Methods.—The procedure originally described[4] as "standard" was used for the preparation of amylsodium at −10° except that *n*-heptane was used as the medium. One-half hour after addition of amyl chloride the 0.5 mole of dried (by heat) halide salt was added. The mixture was then stirred at 10,000 r.p.m. for 90 minutes while the temperature was maintained at −20 to −10°. At the end of that time the rate of stirring was reduced to 5000 r.p.m. and the mixture allowed to warm gradually to 0°. It was then heated quickly (within seven minutes) to 50° where it was cooled to room temperature and the contents of the flask was rinsed with 250 ml. of heptane and the rinsings likewise forced onto solid carbon dioxide. The next day the solids were dissolved by addition of 300–1000 ml. of water, as required. The two layers were separated. The organic layer was extracted with aqueous sodium hydroxide in order to ensure the removal of all acids, dried over magnesium sulfate and then fractionated in order to collect the decane and high-boiling (above 174°) fractions. The aqueous layer was

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[9] A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950); *Rubber Chem. and Tech.*, **24**, 35 (1951).

handled in the usual manner to recover caproic acid and the water-soluble acid.

Chromotropic acid[10] was used to test for formic acid which might have been formed if sodium hydride were produced by pyrolysis, but none was found. Neither was oxalic acid detectable by the use of diphenylamine.[10]

Any tertiary alkoxide used in the work was prepared and added in the manner described in the previous paper[3] and any variation from the conditions given above are indicated in the table.

In all these experiments the propeller blades were three oblique discs approximately 2¹/₈″ long by ¹¹/₁₆″ at the widest point each welded at the center of the straight edge into a slot in the end of the ³/₈″ shaft so that the blades were at a 45° angle from the shaft. This sturdier type of agitator has been used for approximately the last two years in this program of research and gives the excellent agitation needed in much of this work, particularly with granular salts.

Examination of the High-boiling Material.—This material, which was originally collected from 170 to 265°, was refractionated twice in order to collect concentrates of compounds that might be present. Out of 20 g. about 3 g. of material proved to be decane. One fraction (2.3 g.) was reasonably pure di-*n*-amyl ketone, as shown by its identity with an authentic sample in boiling point (55.5° (19 mm.)), refractive index ($n^{25}D$ 1.4250) and the yellow *p*-nitrophenylhydrazone derivative (m.p. 67–88°, reported[11] 68°) which readily decomposed to a red oil on standing overnight. Another fraction (1.2 g.) was largely triamylcarbinol, as judged by the refractive index $n^{25}D$ 1.4453 (reported[12] $n^{20}D$ 1.4470 and boiling point 104° (1 mm.)). Several fractions amounting to 3.7 g. gave a material that boiled 77.5–79.0° (0.15 mm.) and decolorized bromine. All fractions and compounds were analyzed for carbon and hydrogen and found to agree with the formula assigned. These examinations were sufficient to show that the high-boiling material was not derived by polymerization of amyl radicals.

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[10] F. Feigl, "Quantitative Analysis by Spot Tests," 3rd Ed., Trans. by R. E. Oesper, Elsevier Publishing Co., Inc., New York, N. Y., 1946.

[11] A. D. Petrov and E. P. Kaplan, *Izvest. Akad. Nauk U.S.S.R. Otdel Khim. Nauk*, **539** (1949); *C. A.*, **44**, 1887 (1950).

[12] F. C. Whitmore and F. E. Williams, THIS JOURNAL, **55**, 406 (1933).

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Kinetic Evidence for the Triphenylcarbonium Ion as a Reaction Intermediate and Measurement of its Relative Reactivity with Seven Nucleophilic Reagents[1]

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Exceptionally clear evidence for the existence of a carbonium ion intermediate appears in the hydrolysis of 10^{-3} *M* triphenylmethyl (trityl) fluoride, chloride, bromide or thiocyanate in water–acetone solutions. When 10^{-3} *M* azide ion (a strong nucleophilic reagent) is added to any one of these, the rate is unaffected but the product is changed from 100% trityl alcohol to 90% trityl azide. When 10^{-2} *M* chloride ion is added to a 10^{-3} *M* solution of either trityl chloride or bromide, the rate is reduced ("mass effect") to 25% of the rate with trityl chloride alone. By competition experiments, the relative reactivities (*vs.* water) of seven different nucleophilic reagents toward trityl ion have been measured. Trityl ion discriminates much more highly between different nucleophilic reagents than carbonium ions which have a more localized positive charge. Some of the measured relative reactivities are 3.1×10^3 (dimensionless ratio) for chloride ion, 3.7×10^3 for aniline, 5.3×10^4 for hydroxide ion and 2.8×10^5 for azide ion. These figures were affected only slightly by per cent. acetone in the water, temperature and source of trityl ion (from trityl fluoride, chloride or thiocyanate).

Triphenylmethyl (trityl) fluoride liberates fluoride ion in 50% water–50% acetone solution at 25° with a first-order constant ($7.6 \pm 0.4 \times 10^{-4}$ sec.$^{-1}$) *independent* of the concentrations of trityl fluoride (10^{-3} to 10^{-2} *M*) or added sodium fluoride (0 to 3×10^{-3} *M*), sodium hydroxide (0 to 5×10^{-3} *M*), nitric acid (0 to 5×10^{-3} *M*) or sodium azide (0 to 3×10^{-3} *M*). In the absence of added salts, both acid and fluoride ion are produced in 100% yield based on the initial molarity of trityl fluoride, and both are formed at the same rate within the experimental error.

Although the rate is not affected by sodium azide, the product composition is. Adding as little as 1.3×10^{-3} *M* sodium azide decreases to 9.8% the total acid produced indicating the formation of 90% trityl azide. From a reaction with 2×10^{-1} *M* sodium azide, trityl azide, m.p. 58–60°, was isolated in 97% yield. These results can be interpreted only by postulating an unstable intermediate (I) for which water and added anions compete.

$$(C_6H_5)_3CF \xrightarrow[7.6 \times 10^{-4}\ \text{sec.}^{-1}]{k_1,\ \text{slow}} \text{I}$$

$$\text{I} - \begin{cases} \xrightarrow{k,\ Y^-,\ \text{fast}} (C_6H_5)_3Y + F^- \\ \xrightarrow{k^\circ,\ H_2O,\ \text{fast}} (C_6H_5)_3COH + H_3O^+ + F^- \end{cases}$$

Here Y^- may be N_3^-, HO^-, or any nucleophilic reagent capable of yielding a stable product and k° and k are both large second-order rate constants.

It is quite reasonable to write I as

$$(C_6H_5)_3C^{\oplus} + F^{\ominus} \text{ (both ions solvated)}$$

and it is probable in this highly aqueous medium that the ions are dissociated, *i.e.*, that trityl ion is symmetrically solvated by water molecules at the stage where competition with nucleophilic reagents like azide ion occurs.

When only water and azide ion are present

$$\frac{d[(C_6H_5)_3CN_3]}{d[(C_6H_5)_3COH]} = \frac{k_{N_3^-}[N_3^-]}{k^\circ[H_2O]}$$

Integration gives $k_{N_3^-}/k^\circ = ([H_2O]/x) \ln [b/(b - a + x)]$ where b is the initial concentration of azide ion, a is the initial concentration of trityl compound and x is the concentration of acid liberated after ten half-lives.

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[1] This work was supported by the Office of Naval Research, contract no. N5-ori-07838, project no. NR056-198. For full experimental data for runs in 6% water, see K. H. Lohmann, S. B. thesis, M.I.T., May, 1950; for other solvents, see C. B. Scott, Ph.D. thesis, M.I.T., January, 1952.