[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DIFFERENTIAL CLEAVAGE OF THE CARBON TO CARBON LINKAGE BY ALKALI METALS

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Schlenk[1] has shown that dissociable ethanes such as hexaphenylethane react with one per cent. sodium amalgam, forming such colored sodium compounds as triphenylmethyl sodium. Later Ziegler[2] found that the action of the liquid sodium-potassium alloy was so vigorous that even tetraphenylethane was cleaved with the formation of potassium diphenylmethyl. Like the other metallic derivatives this reacted with water, yielding the methane, and with carbon dioxide, forming the salt of diphenylacetic acid.

In a previous paper[3] we have reported the use of Ziegler's reagent in preparing xanthanoic acid from dixanthyl. As would be expected, a similar reaction takes place between the substituted dixanthyls and the alloy.[4] The acids prepared from metallic derivatives from four substituted dixanthyls are reported in the experimental portion of this paper.

Although dibenzyldixanthyl at 25° absorbs oxygen as rapidly as a dissociated ethane, it does not react with one per cent. amalgam in dry ether or benzene even on 24 hours' shaking at room temperature. Under the same conditions in either solvent hexaphenylethane gives a bright red color in five minutes, due to the formation of the metallic derivative. At 80° a solution of dibenzyldixanthyl begins to show a color which fades on cooling. This fact together with its extreme reactivity toward oxygen makes it evident that at room temperature it is either somewhat dissociated in solution or a number of the molecules are in a reactive state closely akin to "real" dissociation. Yet one per cent. sodium amalgam serves to differentiate this compound from hexaphenylethane, which is about 20% dissociated in a dilute solution at 80° and only slightly dissociated at room temperature.[5]

In the hope of finding other reagents that would differentiate between carbon linkages of varying reactivity, we studied 40% sodium amalgam, which is also a liquid at 25°. This reagent reacts with hexaphenylethane and the substituted dixanthyls listed in Table I at room temperature in both ether and benzene. It reacts with dixanthyl at an appreciable rate only in ether and does not react at all with tetraphenylethane.

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[1] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

[2] Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923).

[3] Conant and Garvey, THIS JOURNAL, **49**, 2080 (1927).

[4] Conant and Sloan, *ibid.*, **47**, 572 (1925). Conant and Small, *ibid.*, **47**, 3068 (1925). Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

[5] Gomberg, *Chem. Reviews*, **1**, 107 (1924).

Table I summarizes a series of experiments carried out for the purpose of comparing the reactivity of certain ethanes and dixanthyls. The conditions were as nearly the same as possible in all the experiments and the results are therefore strictly comparable. It is evident that by the use of sodium-potassium alloy and the two liquid sodium amalgams in either benzene or ether it is possible to differentiate between hexaphenylethane, the substituted dixanthyls (with primary groups), dixanthyl, tetraphenylethane and dibenzyl. The differentiation is sharp although it is undoubtedly a question of relative rates of reaction. Thus, although the substituted dixanthyls showed no color with one per cent. amalgam in five minutes or in 24 hours, after many days of continuous shaking a reddish color developed.

TABLE I

THE CLEAVAGE OF CERTAIN COMPOUNDS BY ALKALI METAL

Substance	Na-K ether	Na-K C_6H_6	40% Na-Hg ether	40% Na-Hg C_6H_6	1% Na-Hg ether	1% Na-Hg C_6H_6
Hexaphenylethane	+	+	+	+	+	+
Dibenzyldixanthyl	+	+	+	+	−	−
Di-*n*-butyldixanthyl	+	+	+	+	−	−
Diethyldixanthyl	+	+	+	+	−	−
Dimethyldixanthyl	+	+	+	+	−	−
Dixanthyl	+	+	+	−	−	−
Tetraphenylethane	+	+	−	−	−	−
Dibenzyl	−	−	−	−	−	−

A + sign indicates appreciable cleavage in five minutes as judged by appearance of red color.

A − sign indicates no cleavage in five minutes.

In each case 0.00025 mole of the ethane in 5 cc. of the solvent was shaken with 1 cc. of the liquid metal. The tubes were all shaken violently by hand for five minutes.

The Rate of the Cleavage Reaction Using Sodium-Potassium Alloy

The rate of the cleavage reaction may be followed by either of two methods which give only approximate results. The potassium derivative may be decomposed with carbon dioxide and the resulting acid isolated and weighed. A more rapid method is to titrate the mixture with moist benzene until the color of the metallic derivative disappears. In both methods separate tubes must be used for each time interval. A comparison of the amount of cleavage determined by the two methods with dixanthyl and with tetraphenylethane gave results as follows: (*a*) dixanthyl fast shaking five min., by carbon dioxide 23%, by titration, 13%; (*b*) dixanthyl 50 minutes' slow shaking (on a machine), by carbon dioxide 14%, by titration 4.4%; (*c*) tetraphenylethane 250 minutes' shaking, by carbon dioxide 55%, by titration 45%. The rate of shaking is very important as the results with dixanthyl show and as others with diethyldixanthyl demonstrated; rapid shaking by hand is more effective than the slow shaking of the shaking machine. The amount of alloy and the concentration of the solution are also important. Thus a solution of 0.09 g. of dixanthyl in 5 cc. of ether with 0.25 cc. of alloy required four minutes' shaking for the development of color, with 0.5 cc. of alloy twenty seconds' and with 1 cc. of alloy five seconds'. Because of these variable factors which can be only partially controlled, exact data on the rates of this heterogeneous reaction could not be obtained. In all the comparative experiments we took pains to use the same size and shape of tubes, the same concentration of materials, the same amount of liquid alloy (or amalgam) and to shake in the same manner.

The rates of cleavage of dixanthyl, dimethyldixanthyl, diethyldixanthyl and dibutyldixanthyl were compared using sodium-potassium alloy (1 cc.) and 10 cc. of a 0.025 molar solution. The rate was followed by the titration method and while duplicate determinations in many cases showed considerable divergence the general course of the reaction was evident. (The numerical results are given in the experimental portion of the paper.) Interesting enough, these substances (except dimethyldixanthyl) reacted with sodium-potassium alloy in ether at approximately the same rate. The dimethyldixanthyl reacted at about the same rate as the others during the first five minutes but then the rate fell off rapidly and after 250 minutes only 25% had reacted. It seems probable that with this substance some irreversible rearrangement or decomposition may have been catalyzed by the alloy, and that three-quarters of the material may have been transformed before it had an opportunity of reacting. The reaction of these same compounds with 40% sodium amalgam was so slow that no reliable figures could be obtained; the indications were that the dialkyl dixanthyls reacted about ten times as rapidly as the parent substance.

There might seem to be an inconsistency between the results given in Table I and those mentioned in the preceding paragraph. Forty per cent. sodium amalgam acting on a benzene solution differentiates clearly between dixanthyl and the primary alkyl derivatives. Yet the rates of cleavage by the alloy in ether are not appreciably different. We interpret these results as showing that in the reaction with the alloy the rate-determining process is physical and not chemical, and that only with the 40% amalgam does the difference in reactivity of the compounds manifest itself. It is evident that no heterogeneous reaction involving the mixing of two liquid phases will be likely to proceed instantaneously. The rate will depend on the diffusion of material at the boundary where the reaction proceeds. This rate will be affected by relative volumes, method of mixing and concentrations, as has been noted in our experiments.

The rate of the reaction may also be determined by the solubility of the product and its tendency to cling to the metallic globules. Therefore, the results obtained by using a graded series of reagents (Table I) would be expected to yield more information regarding the rate of the *chemical* reaction than the experiments with sodium-potassium alloy alone.

Experimental

The Formation of Substituted Xanthanoic Acids by Cleavage of Substituted Dixanthyls

One gram of the substituted dixanthyl in 100 cc. of absolute ether was shaken with 10 cc. of sodium-potassium alloy in an atmosphere of nitrogen for 16 hours. The red solution containing a red precipitate was treated with dry carbon dioxide, the alloy removed and the ether layer extracted with water. The aqueous layer was acidified and the precipitated acid purified by recrystallization, usually from a mixture of methyl alcohol and water. The physical properties and analysis of the acids obtained in this way are given in Table II. The methyl esters (also given in Table II) were prepared by the action of dimethyl sulfate on the alkaline solution.

Table II

Compound	Prepared from	M. p. °C.	% C Found	% C Calcd.	% H Found	% H Calcd.	Equivalent weight by titration, NaOH Found	Equivalent weight by titration, NaOH Calcd.	Molecular weight in freezing benzene Found	Molecular weight in freezing benzene Calcd.
Methylxanthanoic acid	Dimethyldixanthyl	205–206	74.8	75.0	5.3	5.0	235	240	...	...
Methyl ester of methylxanthanoic acid	The acid	96–97	76.1	75.6	5.6	5.5	...	...	239	254
Ethylxanthanoic acid	Diethyldixanthyl	173–174	75.9	75.6	5.7	5.5	252	254	...	...
n-Butylxanthanoic acid	Di-*n*-butyldixanthyl	144–145	76.6	76.6	6.5	6.4	286	282	...	...
Methyl ester of *n*-butyl xanthanoic acid	The acid	73–74	77.0	77.0	7.2	6.8	...	...	280	296
Benzylxanthanoic acid	Dibenzyldixanthyl	232	79.7	79.7	5.6	5.1	319	316	...	...
Methyl ester of benzylxanthanoic acid	The acid	103–104	80.0	80.0	6.0	5.5	...	...	314	330

Determination of the Rate of Cleavage

The solution of the material under investigation and the alloy were placed in glass tubes of 15–20 cc. capacity. These were sealed off after filling with dry, oxygen-free nitrogen. (The final purification of the nitrogen consisted in passing it through a solution of sodium triphenylmethyl in ether at 0°.) After shaking (at 23 ± 3°) the tube was placed in a larger cylindrical container of stout glass. This was filled either with dry carbon dioxide or the purified nitrogen, depending on whether the acid was to be isolated or the metallic derivative was to be titrated. By a sharp shake the tube containing the reaction mixture could be broken (a file scratch at the shoulder near the constriction facilitated this operation).

In the titration experiments moist benzene was run in from a buret, the end-point being the disappearance of color. The moisture reacts so much more rapidly with the metallic derivatives than with the alloy that the presence of the latter did not seriously interfere. The benzene was saturated with water at a definite temperature and the solubility of water in benzene as given in Seidell's[6] tables was used in the calculation.

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[6] Seidell, "Solubilities of Organic and Inorganic Compounds," D. Van Nostrand Company, New York, 1919.

In the experiments reported below, 1 cc. of the liquid metal and 10 cc. of the solvent containing 0.00025 mole of the substance were used. All of the tubes were of the same size. They were shaken violently for 30 seconds to disperse the metal and then on the shaking machine for the time indicated. The calculation of the per cent. cleavage from the data is illustrated by the following typical run: 0.09 g. of dixanthyl, 10 cc. of ether, 1 cc. of sodium-potassium alloy, shaken 50 minutes, 6.5 cc. of benzene saturated with H_2O at 23° required; theoretical cc. for complete cleavage 16.7 (at 23° 100 cc. of benzene holds 53.7 mg. of water); per cent. cleaved, 39.0.

Rate of cleavage of **dixanthyl.** With sodium-potassium alloy in ether (the numbers are the per cent. cleavage): 5 min., 39.0, 42.0; 125 min., 71.8, 77.8. With 40% sodium amalgam: 125 min., 1.2; 250 min., 1.4, 1.4. With sodium-potassium alloy in benzene: 250 min., 6.0, 6.8. With 1% amalgam in ether or 40% amalgam in benzene, no perceptible cleavage in 250 min.

Rate of cleavage of **dimethyldixanthyl.** With sodium-potassium alloy in ether: 5 min., 6.2, 6.2; 50 min., 8.6, 12.3; 125 min., 14.2, 16.6; 250 min., 23.3, 24.6. With sodium-potassium alloy in benzene, 250 min., 5.2, 5.2. With 40% amalgam in ether, 250 min., 1.2, 2.0. With 1% amalgam, none in 250 min.

Rate of cleavage of **diethyldixanthyl.** With sodium-potassium alloy in ether: 5 min., 9.9, 15.7; 50 min., 51.1, 47.1; 125 min., 59.9, 69.7. With sodium-potassium alloy in benzene: 125 min., 4.8; 250 min., 5.5, 7.2. With 40% amalgam in ether: 125 min., 3.1; 250 min., 4.9, 10.5. With 40% amalgam in benzene: 250 min., 1.4, 4.8. With 1% amalgam, none in 350 min.

Rate of cleavage of **di-*n*-butyldixanthyl.** With sodium-potassium alloy in ether: 5 min., 1.7, 4.1; 50 min., 42.0, 47.5; 125 min., 63.6, 73.3. With sodium-potassium alloy in benzene: 125 min., 4.2; 250 min., 6.0, 7.5. With 40% amalgam in ether: 125 min., 3.1; 250 min., 2.7, 7.4. With 40% amalgam in benzene: 250 min., 5.5, 6.0. With 1% amalgam in ether, none in 330 min.

Summary

1. The action of sodium-potassium alloy, 40% sodium amalgam and 1% sodium amalgam on a number of substituted dixanthyls and certain ethanes has been studied. By using these reagents in benzene or ether one can differentiate between certain compounds which contain a reactive carbon to carbon linkage.

2. The rate of cleavage by sodium-potassium alloy is essentially the same for a number of substituted dixanthyls and dixanthyl itself. This is probably due to the fact that with this powerful reagent a physical process controls the rate of the heterogeneous reaction.

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