171. *Free Radicals and Radical Stability. Part IX. The Influence of Short-lived and Long-lived Radicals on the Reactivity of Alcohols.*

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A classification of organic compounds according to the unimolecular stability of the constituent radicals is proposed. The study of the chloroformates, carbonates, and formates of short-lived and long-lived hydrocarbon radicals leads to the following rule : The thermal stability of an ester falls with increasing stability of the short-lived radical, and that of an analogous salt rises with increasing stability of the long-lived radical.

A preliminary survey of the behaviour of aryl-substituted methyl alcohols towards liquid potassium shows that the observed reactivity may be expressed as follows : benzyl alcohol < benzhydrol < triphenylcarbinol > diphenyl-*p*-diphenylylcarbinol > diphenyl-α-naphthylcarbinol. It is suggested accordingly that steric as well as electronic influences are operative in this reaction.

A striking feature observed with all the above substances is the remarkably early cessation of the reaction, and the significance of this phenomenon in preparative and analytical work is pointed out.

For some purposes it is convenient to classify organic compounds according to the thermodynamic stability of the constituent radicals. The three classes are made up of the following combinations of radicals : (I) short-lived–short-lived ; (II) short-lived–long-lived ; (III) long-lived–long-lived. The compounds of class I comprise the most widely investigated field of organic chemistry and those of class III have been the subject of much study, but those of class II have received comparatively little attention from the standpoint of thermal stability and reactivity. Actually, this class is of considerable theoretical importance in view of the fact that it bridges the gap between the typical organic compound (class I) and the inorganic-like organic substance (class III) which breaks down spontaneously into stable radicals or ions.

With regard to the behaviour of compounds belonging to class I and class II, the main features relating to the stability of chloroformates and carbonates have been discussed in Part V, and these have been found to correspond with the behaviour of the chloroformates described by Ingold (*J. Soc. Chem. Ind.*, 1939, **58**, 81) and the sulphohalides cited by Le Fèvre (*ibid.*). The more extensive study of formates containing unsubstituted hydrocarbon radicals (Part VIII) now enables us to embody the previous findings in the rule enunciated in the summary.

It is shown in Part VIII (preceding paper) that the reduction of carbinols by formic acid proceeds in virtue of the thermal decomposition of the triarylmethyl formate, and does not involve the hydroxyl group except in so far as the initial process of salt formation is concerned. Apart from the qualitative studies of Baeyer and Villiger (*Ber.*, 1902, **35**, 3013), the information available regarding the reactivity of class II compounds is extremely meagre. In view of the extensive use of alkoxides in preparative work, and the fact that no quantitative studies have been made on the reactivity of alcohols towards alkali metals, we have made a preliminary survey of the action of metallic potassium on the aryl-substituted methyl alcohols in xylene solution. On account of the heterogeneous nature of the reaction system and the physical peculiarities of molten potassium, the method offers several practical difficulties, but it possesses the advantage of directness and furnishes a means of comparing the effect of substituted methoxyl radicals on the reactivity of the hydrogen atom.

For reasons mentioned later, it is necessary to compare the early stages of the reactions, and on this basis, the rate of evolution of hydrogen may be expressed as follows: benzyl alcohol 6·5, benzhydrol 11·2, triphenylcarbinol 14·8, diphenyl-*p*-diphenylylcarbinol 13·7, diphenyl-α-naphthylcarbinol 9·3. Conductivity measurements in non-polar solvents reveal that all these alcohols are un-ionised, but the genesis of new properties in triphenylcarbinol is evident from the fact that all fully arylated carbinols ionise in liquid sulphur dioxide to form coloured solutions and give halochromic salts with strong inorganic and organic acids. These reactions, however, arise from the stability characteristics of the long-lived triarylmethyl cation R_3C^+, and thus differ essentially from the present reaction which involves the behaviour of hydrogen covalently linked to the arylated methoxyl radical $R_3C{-}O{-}$. All the simple arylated methoxyl radicals are short-lived, and since the stabilising requirements of tervalent carbon and univalent oxygen are essentially different, it is not surprising that the reactivity of the hydroxyl hydrogen varies inversely as the unimolecular stability of the triarylmethyl radical. This behaviour may also be interpreted as being due to steric hindrance, and we incline to the view that such factors (arising from the large size of the aryl groups) are also operative in this reaction.

A striking feature of the reaction is the comparatively sudden cessation of the substitution process in the presence of a large excess of metal. This remarkable phenomenon has also been observed by Brönsted and Kane (*J. Amer. Chem. Soc.*, 1931, **53**, 3631) in the reaction of liquid amalgams with dilute acids and by Fraenckel and Heinz (*Z. anorg. Chem.*, 1924, **133**, 153) with strong acids. This feature is of considerable significance in the preparation of alkoxides, in the drying of organic solvents, and in the estimation of water in organic liquids by the sodium–potassium method.

EXPERIMENTAL.

Potassium was chosen as reacting metal in these experiments in view of its low m. p. and of the fact that the potassium alkoxides, unlike the corresponding lithium and sodium derivatives (Part VI), are readily soluble in hot xylene. Complications arising from the presence of a solid phase are thus avoided, and the system preserves its diphasic character throughout the reaction.

Preparation of Materials.—Xylene was purified by prolonged refluxing over sodium and then over potassium in an atmosphere of nitrogen; it was distilled over potassium immediately before use. The alcohols were purified and rigorously dried by standard methods. The carbinols were purified by repeated crystallisation from sodium-dried ligroin, and the finely-powdered specimens were dried for 18 hours over sulphuric acid.

Rate of Evolution of Hydrogen.—The reaction vessel was similar to a Beckmann tube (15 × 1·7 cm.) with the main side tube fitted with a device for precipitating the substance under investigation into the solvent. A long vertical tube was fused to the main side tube and communicated with a gas burette charged with xylene. The neck of the reaction vessel was closed by a stopper carrying a mercury-sealed glass stirrer operated by a motor, and the speed of stirring was adjusted to a predetermined value as registered by a magnetic speed indicator. In this manner a high constant rate of stirring could be maintained throughout the reaction and could be duplicated in the several experiments.

The reaction vessel, charged with xylene (15 c.c.) and metallic potassium (1·262 g.; 10 atoms), was securely clamped in a thermostat maintained at 100° ± 0·05°, and the air displaced by means of dry nitrogen. A known weight of the carbinol (1 mol.) was placed in the precipitating device, and the stirrer set to operate at the desired speed (3 revs. per sec.). The carbinol was precipitated into the xylene–potassium mixture, and the volume of evolved hydrogen observed at intervals. A selection of typical results, in which the volumes have been reduced to N.T.P., is given below, *t* being the time in minutes.

Interaction with Potassium.

t.	H_2 (c.c.).	*t*.	H_2 (c.c.).	*t*.	H_2 (c.c.).	*t*.	H_2 (c.c.).	*t*.	H_2 (c.c.).	*t*.	H_2 (c.c.).
Benzyl alcohol (0·3487 g.).						*Benzhydrol* (0·5940 g.).					
1	6·48	6	13·05	16	15·52	1	11·18	9	18·20	25	20·08
2	9·24	8	14·47	18	15·63	2	13·46	11	19·04	30	20·28
3	10·67	10	14·86	20	15·63	3	14·40	15	19·52	35	20·28
4	11·24	12	15·24	25	15·63	7	17·85	20	19·90	40	20·28
5	12·19	14	15·43								
Triphenylcarbinol (0·8387 g.).						*Diphenyl-*p*-diphenylylcarbinol* (1·0844 g.).					
1	14·81	6	23·43	11	25·31	0·5	12·03	3	14·99	7	15·47
2	18·19	7	24·08	12	25·36	1	13·75	4	15·28	8	15·47
3	20·44	8	24·65	15	25·36	1·5	14·32	5	15·45	10	15·47
4	21·84	9	24·98	20	25·36	2	14·61				
5	22·88	10	25·12								
Diphenyl-α-naphthylcarbinol (1·000 g.).											
1	9·32	2	10·16	3	10·44	4	10·63	5	10·73	10	10·73

A high speed of stirring was found to be essential in order to obtain reproducible results, but some of the observed variations are undoubtedly due to the breaking-up of the liquid metal into globules of different size. Although this effect is unavoidable owing to the different interfacial tensions between the metal and the solutions, the variations have been reduced as far as possible by the use of a large excess of the metal. Actually, this effect was least marked with the carbinol solutions, and in these cases the differences in the observed rates are undoubtedly due to chemical factors.

A noteworthy feature of the above reactions is the very early and comparatively sudden cessation of the evolution of gas. After the initially vigorous stage, the evolution of hydrogen falls off rapidly, and the reaction soon stops completely. This behaviour is exhibited by all the above alcohols, but is most prominent in the derivatives of high molecular weight. The existence of a well-defined critical concentration at which no further reaction apparently occurs is doubtless connected with the mass-action effects which obtain in the interfacial layer, and is probably to be referred to the lower availability of the hydroxyl group as a result of the lower adsorbability of the larger molecules or the operation of steric factors in the adsorption layer. This phenomenon is of importance in many preparative processes and furnishes the basis for the customary practice of using a large excess of alcohol in the preparation of alkoxides.

The present experiments also throw some light on the analytical methods which have been proposed for the estimation of dissolved water in organic solvents by the use of sodium–potassium alloy. The effect under discussion does not appear to have been considered in this connexion, but it is evident that the method cannot give the true water content of the system. Similar remarks apply to the drying of organic solvents by sodium, which effects only partial decomposition of the water dissolved in a liquid phase. The drying process can be rendered more efficacious by distilling the liquid through a column containing freshly-drawn sodium wire, as we have already shown in the drying of ether for the preparation of Grignard derivatives of complex halogen compounds (Part IV), which are difficult or impossible to prepare by the use of ether dried in the ordinary way.

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