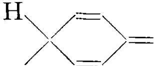
# 43. *Free Radicals and Radical Stability. Part VII. The Influence of the Phenoxyl Group on the Stability of Ketylic Derivatives. The Preparation of Carbon Monoxide from Carbonates.*

By Sydney T. Bowden and Tudor John.

Carbon monoxide is evolved when phenyl carbonate is treated with metallic sodium. The only other product is sodium phenoxide, and the over-all reaction may be represented as $Ph_2CO_3 + 2Na = 2PhONa + CO$. The gas is 100% pure, and since it is formed in a system containing free sodium, it does not explode when sparked with dry oxygen. The reaction thus furnishes a convenient and rapid method of preparing carbon monoxide in a sufficiently dry condition for demonstrating the catalytic effect of moisture on combustion.

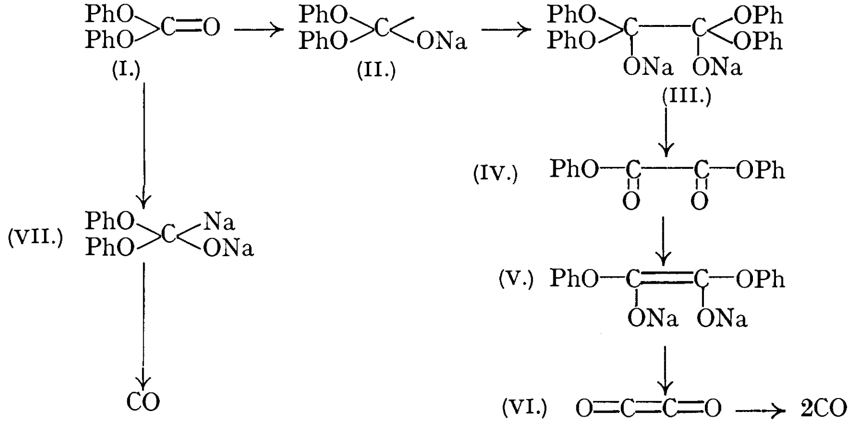
The mechanism of the reaction under the specified conditions is briefly discussed. The absence of colour in the reaction mixture, and the fact that a similar reaction occurs with aliphatic derivatives such as ethyl carbonate, would seem to point to simple scission of the carbonate. If, however, the reaction actually involves the ketyl mechanism, as found in the case of other esters, then the ketyl system formed from the carbonate must either be colourless or suffer rapid transformation into a colourless intermediate which subsequently eliminates sodium alkoxide or aryloxide.

The formation of sodium triphenylmethoxide through the condensation of ethyl carbonate and chlorobenzene in the presence of sodium is readily explained on the basis of the ketyl mechanism.

The influence of the phenoxyl group on the unimolecular stability of free radicals has been studied by Wieland (*Ber.*, 1911, **44**, 2550), who found that the dissociation of tetraphenyldiphenoxyethane into diphenylphenoxymethyl occurs to a much smaller extent than that of hexaphenylethane into triphenylmethyl. The inhibitory influence of the phenoxyl group in this connexion reveals that the capacity of a phenyl group for stabilising the electronic state of the methyl carbon atom is greatly diminished by the interposition of an oxygen atom. In view of recent work on free radicals of the ketyl type (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 1179; Doescher and Wheland, *ibid.*, 1934, **56**, 2011; Sugden, J., 1936, 440), the influence of the phenoxyl group on the unimolecular stability of these radicals is of considerable interest. We have, however, no direct information on this point, for, as Blicke (*J. Amer. Chem. Soc.*, 1924, **46**, 2561) has shown, the associated derivatives of the type $[CPh(OPh)(ONa)]_2$ are unstable and spontaneously eliminate sodium phenoxide. It was found, however, that an ethereal solution of phenyl benzoate reacts with sodium to produce a deep red solution before precipitation of the phenoxide occurs. The intense colour was attributed to the presence of the ketyl  =C(ONa)(OPh) produced through quinoidation of the phenyl group. For the purpose of obtaining further information with regard to the rôle of the phenoxyl group and avoiding at the same time direct quinoidation effects, we have now examined the action of sodium on dipolar carbonates of the general formula $CO(OR)_2$.

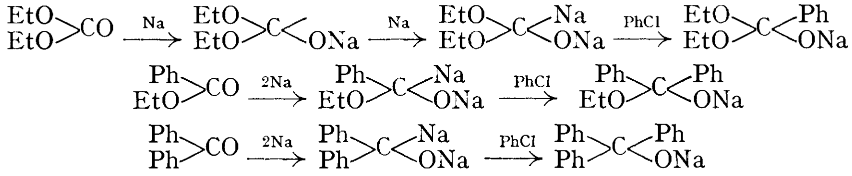
When metallic sodium is added to a xylene solution of phenyl carbonate, a slow evolution of carbon monoxide sets in even at room temperature; when the solution is warmed, the reaction proceeds briskly and sodium phenoxide is deposited as a semi-gelatinous precipitate. If the reaction is carried out with one atomic equiv. of sodium, roughly half of the carbonate is decomposed, but with two atomic equivs., most of the metal disappears and the decomposition of the carbonate is practically complete. Owing to the heterogeneous nature of the system the speed of the reaction is greatly influenced by agitation, and stirring at 110° affords nearly 80% of the theoretical amount of carbon monoxide in the course of an hour. Inasmuch as the reaction proceeds smoothly and the gas is obtained in a high state of purity, the method is well suited for the laboratory preparation of carbon monoxide. Thus prepared, the gas is so dry that it does not explode on sparking with dry oxygen, and may therefore be used directly for demonstrating the catalytic influence of moisture on the combustion of carbon monoxide.

The decomposition of the carbonate may involve simple scission of the type observed by Schorigin (*Ber.*, 1926, **59**, 2510) in the case of ethers : $CO(OPh)_2 + 2Na = NaOPh + Ph{\cdot}CO_2Na \longrightarrow NaOPh + CO$, and it is significant in this connexion that the solution remains colourless throughout except for the production of a slight yellow colour towards the end of the reaction. However, the carbonic ester (I) contains a carbonyl group, and the reaction with alkali metal may thus be expected to occur in analogous manner to that found for the esters of monobasic organic acids. On these premises the initial reaction involves the formation of the ketyl (II), which suffers partial dimerisation (Bachmann, *loc. cit.*) to (III). The latter, however, is thermally unstable (Blicke, *loc. cit.*) and eliminates two molecules of sodium phenoxide to produce the compound (IV), which reacts in turn with sodium to form the disodium derivative (V). The further elimination of sodium phenoxide leads to the formation of dicarbon dioxide (VI), which is unstable under these conditions and breaks down into carbon monoxide. Jones and Tasker (J., 1909, **95**, 1904) tried to prepare the oxide $C_2O_2$ by the interaction of sodium phenyl mercaptide and oxalyl chloride, but failed. A further attempt to prepare the gas by the action of oxalyl chloride on nickel carbonyl gave only carbon monoxide.



Since the reaction of sodium with phenyl carbonate involves two atoms of the metal, it is possible that the disodium derivative (VII) is also formed and that it decomposes directly into sodium phenoxide and carbon monoxide. One of the chief characteristics of the simple ketyls is found in the intense colours produced in ethereal solution, and the absence of colour in the system under study would seem to indicate that the reaction does not proceed through the ketyl mechanism. However, it has been shown by Wooster and Dean (*J. Amer. Chem. Soc.*, 1935, **57**, 112) that the reactions and electrolytic properties of metal ketyls are consistent with the equilibrium $CR_2Na{\cdot}O{\cdot} \rightleftharpoons {\cdot}CR_2{\cdot}ONa$, and it is evident that such an equilibrium will largely depend on the nature of the solvent. Phenyl benzoate, for example, is immediately attacked by sodium when dissolved in ether but not in benzene. This, together with the fact that the quinoidation effects responsible for the production of colour may be largely repressed in non-polar solvents, leads us to conclude that the ketyl system may be colourless under certain conditions. Accordingly, the absence of colour cannot be taken as proof that the reaction does not proceed through the ketyl mechanism. Apart from the influence of the solvent, the nature of the group R will determine the electronic condition of the carbon atom, and it appears, therefore, that the ketyl produced from phenyl carbonate must either be colourless or suffer immediate transformation into a colourless derivative which subsequently eliminates sodium phenoxide. It may be noted that Blicke (*loc. cit.*) has found that ethyl trimethylacetate in ethereal solution reacts with sodium to form colourless products, although coloured ketyls of the aliphatic series have been described by Favorsky and Nazorov (*Bull. Soc. chim.*, 1934, **1**, 46). We find that sodium reacts with ethyl carbonate with evolution of carbon monoxide, and that the solution is practically colourless throughout the reaction.

The condensation of ethyl carbonate with chlorobenzene in the presence of metallic sodium has been examined by Morton and Stevens (*J. Amer. Chem. Soc.*, 1931, **53**, 4030), who found that sodium triphenylmethoxide is the chief product. On the basis of the ketyl mechanism adumbrated above, the formation of triphenylcarbinol may be explained in accordance with the following scheme :



$$\begin{matrix}\mathrm{EtO}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{CO} \xrightarrow{\mathrm{Na}} \begin{matrix}\mathrm{EtO}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\\\mathrm{ONa}\end{matrix} \xrightarrow{\mathrm{Na}} \begin{matrix}\mathrm{EtO}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{Na}\\\mathrm{ONa}\end{matrix} \xrightarrow{\mathrm{PhCl}} \begin{matrix}\mathrm{EtO}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{Ph}\\\mathrm{ONa}\end{matrix}$$

$$\begin{matrix}\mathrm{Ph}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{CO} \xrightarrow{2\mathrm{Na}} \begin{matrix}\mathrm{Ph}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{Na}\\\mathrm{ONa}\end{matrix} \xrightarrow{\mathrm{PhCl}} \begin{matrix}\mathrm{Ph}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{Ph}\\\mathrm{ONa}\end{matrix}$$

$$\begin{matrix}\mathrm{Ph}\\\mathrm{Ph}\end{matrix}\!>\!\mathrm{CO} \xrightarrow{2\mathrm{Na}} \begin{matrix}\mathrm{Ph}\\\mathrm{Ph}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{Na}\\\mathrm{ONa}\end{matrix} \xrightarrow{\mathrm{PhCl}} \begin{matrix}\mathrm{Ph}\\\mathrm{Ph}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{Ph}\\\mathrm{ONa}\end{matrix}$$

In support of this hypothesis, it is significant that Frey (*Ber.*, 1895, **28**, 2520) and Morton and Stevens (*loc. cit.*) have shown that benzophenone, chlorobenzene, and sodium react in ethereal solution to produce sodium triphenylmethoxide in almost quantitative yield.

## EXPERIMENTAL.

*Action of Sodium on Phenyl Carbonate.*—Phenyl carbonate was prepared by the action of carbonyl chloride on sodium phenoxide (Hentschel, *J. pr. Chem.*, 1883, **27**, 41) and was purified by recrystallisation from alcohol and finally from dry ligroin with adequate precautions against the intrusion of moisture.

(*a*) Phenyl carbonate (1 g.) was dissolved in sodium-dried xylene (10 c.c.) in a small flask provided with a side tube (for the admission of dry nitrogen) and a reflux condenser fitted with a guard-tube containing anhydrous calcium chloride and soda-lime. On the addition of shavings of metallic sodium (0·12 g., 1 atom), a slow evolution of gas set in after a few minutes. The reaction was accelerated by warming the mixture, and a white semi-gelatinous solid was soon deposited from solution. After the solution had been boiled until the metal had disappeared, it was allowed to cool and was then filtered through a sintered-glass filter under dry nitrogen. The solid was triturated with light petroleum and dried over sulphuric acid and silica-gel (Found : Na, 19·87. Calc. for $C_6H_5$·ONa : Na, 19·83%). The identity of the substance was further established by the formation of tribromophenol on treatment with bromine, and by its reconversion into phenyl carbonate by the action of carbonyl chloride.

The original filtrate was evaporated in a desiccator containing silica gel, and the white residue thus obtained did not appreciably lower the m. p. of an authentic specimen of phenyl carbonate. The amount of carbonate thus recovered was 0·4 g.

(*b*) In a similar experiment using 2 atom-equivs. of sodium, prolonged boiling of the mixture led to the formation of the same products and almost complete disappearance of the metal. The final solution, however, was pale yellow after this treatment, and only a trace of phenyl carbonate was recovered.

(*c*) The experimental arrangement was modified so that the evolved gas was collected over mercury in an explosion burette. By exploding the mixture of the gas and moist air, it was shown to be pure carbon monoxide (100%). Although the gas burned in the ordinary air with a blue, lambent flame, it is noteworthy that on several occasions we were unable to explode a mixture of the gas with oxygen which had been dried simply by passage through concentrated sulphuric acid.

(*d*) The following preliminary experiments were carried out in order to obtain information concerning the rate of the reaction. The reaction vessel consisted of a Pyrex test-tube (2·5 cm. in diameter) which was closed with a rubber stopper carrying a mercury-sealed glass stirrer,

*Evolution of carbon monoxide.*

Experiment I.

| Time (mins.) | 2 | 5 | 10 | 20 | 30 | 40 | 60 | 100 | 150 | 210 |
|---|---|---|---|---|---|---|---|---|---|---|
| Volume (c.c.) | 3·5 | 7·2 | 11·4 | 18·6 | 22·4 | 25·2 | 31·8 | 40·9 | 49·9 | 60·7 |

Experiment II.

| Time (mins.) | 1 | 2 | 3 | 4 | 8 | 12 | 16 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Volume (c.c.) | 12·0 | 23·3 | 29·8 | 33·8 | 43·3 | 49·1 | 53·9 | 57·6 | 65·5 | 68·2 | 73·2 | 75·3 |

Volume evolved for complete reaction = 104·6 c.c.

while a side tube communicated (*via* a short water-cooled reflux condenser) with a gas burette filled with mercury. The vessel containing a solution of phenyl carbonate (1 g.) in xylene (15 c.c.) was placed in a thermostat at 110°, and metallic sodium (0·215 g., 2 atoms), supported in a glass basket within the apparatus, was precipitated into the solution. The gas evolved was collected in the gas burette and the volume measured at definite intervals. In the first experiment the mixture was not stirred mechanically, but in the second experiment stirring was effected by two vertical glass rods fused to a spindle which was rotated at 180 r.p.m. by means of a motor.

The table shows that the speed of the reaction is greatly affected by stirring the mixture, and it is evident that the process not only facilitates diffusion at the reaction interface, but also serves to break up the molten metal into globules which offer a fresh reaction surface. The latter effect is partly responsible for the fact that the rate of evolution of the gas does not conform very closely with any of the simple kinetic equations.

For the ordinary laboratory preparation of the gas it is advisable to employ excess of sodium and finally to boil the solution in order to avoid the use of stirring apparatus. A solution of phenyl carbonate (15 g.) in 150—200 c.c. of xylene is placed in a round-bottomed flask provided with a short reflux condenser connected directly to the gas-collecting unit. Excess sodium (about 4 g.) is added, and the mixture is gradually heated on an electric heater or sand-bath. The evolution of gas may be controlled by regulating the rate of heating, and it is advisable to heat very slowly as the m. p. of the metal is approached. The reaction proceeds briskly when the metal is in the molten condition, but may, if necessary, be further accelerated by raising the temperature to the b. p. of the solution. With the above quantities, 1 l. of pure carbon monoxide may be collected in less than an hour.

*Action of Sodium on Ethyl Carbonate.*—A solution of freshly distilled ethyl carbonate (1 g.) in xylene was heated with metallic sodium (0·39 g., 2 atoms) in the apparatus described above. Carbon monoxide was evolved, and sodium ethoxide was deposited as a brownish gelatinous solid. After the solution had been kept at 110° for 2 hours, most of the metal had disappeared and the volume of carbon monoxide evolved was practically quantitative. The action of sodium on this aliphatic derivative is therefore essentially similar to that found in the case of phenyl carbonate.

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