XC.—*The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. Part II. The Influence of the Hydroxy-compound.*

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In Part I (J., 1924, **125**, 115) an account was given of the reaction between phenylmethylcarbamyl chloride and ethyl alcohol at different temperatures. An account is now given of the reaction between phenylmethylcarbamyl chloride and various hydroxy-compounds at 100°.

Norris and Ashdown (*J. Amer. Chem. Soc.*, 1925, **47**, 837) studied the reaction between various alcohols and *p*-nitrobenzoyl chloride in ether at 25°, but no quantitative work, so far as the author is aware, has hitherto been published on the influence of the constitution of the hydroxy-compound upon the velocity of reaction with a carbamyl chloride.

Materials.—The phenylmethylcarbamyl chloride was from the same batch as was used in the previous work, and had been kept over phosphoric oxide in a desiccator.

The various alcohols used were the purest commercial alcohols and were all treated twice at their respective boiling points with fresh calcium turnings (1·0 and 0·5% by weight) and fractionated. The other hydroxy-compounds, which also were the purest commercial substances, were purified by fractional distillation, some under reduced pressure. Each hydroxy-compound after purification boiled either constantly at one temperature or over a range of less than 0·2°.

Method of Work.—In each experiment, 0·424 g. of the carbamyl chloride (equivalent to 25 c.c. of *N*/10-solution) and 5 c.c. of the hydroxy-compound were sealed in a test-tube and heated at 100° for a definite time. A hydroxy-compound that was solid at the ordinary temperature was first melted and 5 c.c. were placed in the tube, which was then cooled before the carbamyl chloride was introduced. These proportions caused the hydroxy-compound to be present in large excess, thus making the reaction unimolecular with respect to the carbamyl chloride.

In the case of the alcohols the whole reaction is made up of two consecutive reactions :

$$(1)\ \mathrm{NMePh{\cdot}COCl + ROH = NMePh{\cdot}CO_2R + HCl}$$
$$(2)\ \mathrm{HCl + ROH = RCl + H_2O}$$

but the progress of the first reaction can be studied by determining the amount of carbamyl chloride left in the system at any instant. This was done, for those alcohols (methyl, ethyl, and *n*-propyl) which give low-boiling chlorides, in the manner described in Part I (*loc. cit.*). For the other hydroxy-compounds, since aspiration of air through the system would not remove the chloro-compound formed, the following method was used. After being heated at 100° for the required time, the mixture was titrated with *N*/10-potassium hydroxide Excess of ammonia was then added to convert any unchanged carbamyl chloride into ammonium chloride and the corresponding substituted carbamide. The solution, after standing in the cold for 1 hour to complete the conversion, was extracted four times with light petroleum to remove the chloro-derivative of the hydroxy-compound, acidified with pure nitric acid, and titrated with *N*/10-silver nitrate without an indicator. This titre was a measure of both the ammonium chloride and the hydrogen chloride present. The amount of the latter was known from the *N*/10-potassium hydroxide titre, and by subtraction the ammonium chloride titre, which was equivalent to the carbamyl chloride, was obtained.

In the case of *n*-propyl alcohol both methods were employed, and gave almost identical results.

The quantity of phenylmethylcarbamyl chloride present being known, the velocity coefficient for a unimolecular reaction was calculated from the expression

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

where t_1 is 5 minutes and $a - x_1$ is the amount of carbamyl chloride present in the system after the tube had been in the water-bath at 100° for 5 minutes. This expression was used to obviate the initial disturbances.

Results.

In Table I, where the results for methyl and *n*-propyl alcohols are given in detail, the first column gives the duration of heating in minutes (*t*), the second the amount of hydrogen chloride present, expressed as c.c. of *N*/10-solution (*b*), the third the amount of hydrogen chloride plus phenylmethylcarbamyl chloride present, expressed as c.c. of *N*/10-solution (*c*). The fourth column gives the amount of phenylmethylcarbamyl chloride present (*d*), obtained by subtracting the figures in column 2 from those in column 3. The fifth column gives the velocity coefficient for the reaction between phenylmethylcarbamyl chloride and the hydroxy-compound, calculated from the figures in column 4.

The whole of the results are summarised in Table II.

TABLE I.

Methyl Alcohol.					n-*Propyl Alcohol.*				
t.	*b.*	*c.*	*d.*	*k.*	*t.*	*b.*	*c.*	*d.*	*k.*
5	12·44	23·52	11·00	—	5	1·46	25·02	23·56	—
6	13·83	22·57	8·74	0·237	10	3·96	24·90	20·94	0·0236
8	14·96	20·59	5·63	0·216	15	6·49	24·71	18·22	0·0257
10	15·05	18·61	3·56	0·227	20	8·14	24·48	16·34	0·0244
13	14·18	16·18	2·00	0·214	25	9·81	24·11	14·30	0·0250
15	13·06	14·34	1·28	0·216	35	11·98	23·15	11·17	0·0249
			Mean	0·222	45	13·76	21·96	8·20	0·0264
					60	14·74	20·47	5·73	0·0257
								Mean	0·0251

TABLE II.

Hydroxy-compound.	Limits of *k*.	Mean *k*.
$CH_3{\cdot}OH$	0·237 —0·214	0·222
$C_2H_5{\cdot}OH$	0·0437—0·0417	0·0427
$n\text{-}C_3H_7{\cdot}OH$	0·0264—0·0236	0·0251
$iso\text{-}C_3H_7{\cdot}OH$	0·0113—0·0099	0·0106
$n\text{-}C_4H_9{\cdot}OH$	0·0188—0·0166	0·0177
$iso\text{-}C_4H_9{\cdot}OH$	0·0158—0·0154	0·0156
$iso\text{-}C_5H_{11}{\cdot}OH$	0·0125—0·0121	0·0123
$CH_2Ph{\cdot}OH$	0·0198—0·0179	0·0185
$CH_2{:}CH{\cdot}CH_2{\cdot}OH$	0·0448—0·0399	0·0420
$CHPh{:}CH{\cdot}CH_2{\cdot}OH$	0·0078—0·0068	0·0074
PhOH	0·317 —0·290	0·308
$o\text{-}C_6H_4Me{\cdot}OH$	0·0567—0·0514	0·0541
$m\text{-}C_6H_4Me{\cdot}OH$	0·149 —0·139	0·146
$p\text{-}C_6H_4Me{\cdot}OH$	0·176 —0·169	0·175
$C_2H_4(OH)_2$	Too fast to measure accurately.	
$C_3H_5(OH)_3$	Did not dissolve the carbamyl chloride.	

The hydroxy-compound may influence the reaction in two ways : by its constitution and by its solvent action. The influence of a solvent on the velocity of a reaction in which it does not take part has been extensively studied, and no general relation has been traced between the chemical or physical properties of the solvent and its effect on the velocity coefficient.

Menschutkin (*Z. physikal. Chem.*, 1887, **1**, 611; 1890, **6**, 41) found that the velocity of certain reactions was greatest in those solvents having the highest dielectric constant, but in other reactions this rule did not hold. Patterson and Montgomerie (J., 1912, **101**, 26, 2100) state that a given set of solvents may hasten a particular reaction in a certain sequence, whilst it may retard another reaction in the same or nearly the same sequence, and that the properties which bring this about are probably the same throughout.

Another view of the influence of the solvent is that the solvent and the solute form an unstable additive compound, in which case it is probable that the chemical constitution of the solvent, rather than its physical properties, would be most effective in influencing the velocity of the reaction. The work of Cox (J., 1920, **117**, 493) supports this view.

In the present work, the hydroxy-compound, which can be regarded as a solvent, reacts with the carbamyl chloride, hence its chemical constitution does influence the velocity of the reaction and the question arises whether, in addition to that, the physical properties of the hydroxy-compound play a part. The physical properties most likely to have some effect upon the velocity of a reaction are the viscosity, the dielectric constant, and the refractive index.

Reformatsky (*Z. physikal. Chem.*, 1891, **7**, 34) showed that viscosity did not appear to have any great influence on the velocity coefficient of a reaction. The refractive index of the hydroxy-compounds examined varies between $n_D^{20^\circ}$ 1·3290 for methyl alcohol and $n_D^{26 \cdot 6^\circ}$ 1·576 for cinnamyl alcohol; for most of them it is about 1·4, so that the small differences in refractive index are not sufficient to explain the large differences in velocity coefficient. The dielectric constant shows a greater variation, the highest being 32 for methyl alcohol (20°) and the lowest 9·7 for phenol (48°). These two extremes, however, are the values for the hydroxy-compounds having the greatest velocity coefficients, so that there does not seem to be a connexion between dielectric constant and velocity coefficient. In addition, the differences between the physical properties of the various liquids will tend to become smaller as the temperature is raised and therefore it is probable that at 100° the effect due to the different solvent action of the hydroxy-compounds will be very small compared with the effect of their differences in chemical constitution.

In considering the effect of chemical constitution upon the velocity of a reaction several factors have to be taken into account: first, the general polar effect, due to substituent atoms or groups affecting the molecule as a whole; secondly, the steric effect; and thirdly, an alternate polarity effect. In many cases two or all three factors may operate simultaneously, and then it is difficult to assess the effect of each factor individually. With regard to the straight-chain aliphatic primary alcohols, the steric factor is not sufficiently strong to influence the velocity, and the results show no trace of an alternate effect, for the velocity coefficients are in the order methyl alcohol > ethyl alcohol > *n*-propyl alcohol > *n*-butyl alcohol. The order is the same as that found by Menschutkin (*Z. physikal. Chem.*, 1887, **1**, 611) in the reaction between acetic anhydride and several alcohols in benzene solution at 100°, and different from that found by Norris and Ashdown (*loc. cit.*), where the order was methyl alcohol > ethyl alcohol > *n*-butyl alcohol > *n*-propyl alcohol. The reactivity of the alcohol decreases, *i.e.*, the hydroxyl hydrogen atom becomes more firmly bound, as the length of the straight chain increases. With the primary *iso*-compounds it is again seen that an extra $-CH_2-$ group in the straight chain decreases the velocity coefficient. A branched-chain alcohol has a smaller velocity coefficient than a straight-chain alcohol of the same molecular weight; thus *n*-propyl > *iso*propyl and *n*-butyl > *iso*butyl. In the case of *iso*propyl alcohol the velocity coefficient is abnormally small, probably owing to a steric effect superimposed upon the general polar effect of the substituent, since this is a secondary alcohol whilst the others are primary alcohols. A similar effect was found by Ashdown and Norris.

The introduction of a phenyl group at the end of the straight chain decreases considerably the reactivity of the alcohol, as is shown by the following figures: methyl alcohol 0·222, benzyl alcohol 0·0185, allyl alcohol 0·0420, cinnamyl alcohol 0·00744.

The effect of unsaturation is to cause a great increase in the reactivity of the alcohol; thus *n*-propyl alcohol 0·0251, allyl alcohol 0·0420.

Taking methyl alcohol as the standard, and considering the replacement of one of its hydrogen atoms in the methyl group, we find that the general polar effect of the various substituents in decreasing the reactivity of the hydroxyl hydrogen is in the following order: $CH_3 < CH_2{:}CH < C_2H_5 < C_6H_5 < C_3H_7 < CH(CH_3)_2 < CH(CH_3)_2{\cdot}CH_2 < C_6H_5{\cdot}CH{:}CH$.

The introduction of a second hydroxyl group, as in ethylene glycol, increases the reactivity so greatly that the velocity coefficient cannot be obtained with accuracy by the method employed.

The aromatic compounds show special features. Phenol, as was to be expected, is very reactive, more so than methyl alcohol. The introduction of a methyl group, as in the cresols, diminishes the reactivity of the hydroxyl hydrogen, the extent of the diminution depending on the relative positions of the methyl and hydroxyl groups in the benzene ring. The velocity coefficients are: phenol 0·308, *o*-cresol 0·0541, *m*-cresol 0·146, *p*-cresol 0·175. The low value for *o*-cresol is undoubtedly due to a preponderating steric effect.

Work with other carbamyl chlorides is in progress.

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