# **265.** *The Second (Rapid) Step in the Nucleophilic Substitution of Alkyl Halides. Part II.* Competitive Substitution Reactions.*

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The course of competitive substitution reactions of some alkyl halides is outlined, in which an ionic substituent (azide or thiocyanate) competes with a molecular one (water) for the same carbonium ion (triphenylmethyl, diphenylmethyl, di-*p*-tolylmethyl) yielding the alkyl azide or thiocyanate and the alcohol, which are all stable. The combination of the solvents and presence of various additives affect differently the activities of the reacting species and, in particular, that of the carbonium ion and ionic substituent. This is established by analysis. Decrease in dielectric constant usually increases the ratio of alkyl azide (thiocyanate) to alcohol; increase of ionic strength decreases it.

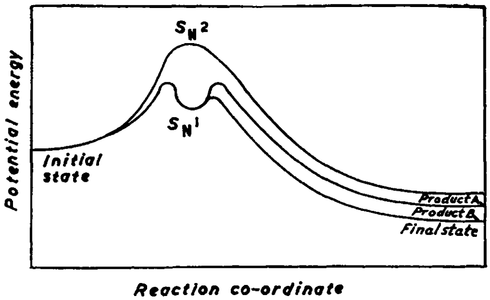
For the hydrolysis of triphenylmethyl chloride, a scheme was adopted * according to which two substituting agents—one molecular and one ionic—compete for the carbonium ion, but only one product is obtained—the alcohol; the other reaction is the reassociation between the carbonium and the halide ion. Yet the kinetic process is complicated by this competition to an extent indicated by $\alpha = k_2/k_3$, the ratio of the rates of the competing reactions.

If we add some other ionic substituent to the reaction mixture, say azide ions, three substituents (halide, azide, and water) compete for the carbonium ion, yielding the corresponding alcohol and alkyl azide, which are both stable:[1,2]

$$RX \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R^+ + X^-; \quad R^+ + N_3^- \xrightarrow{k_2'} RN_3; \quad R^+ + H_2O \xrightarrow{k_3} ROH \ . \qquad (1)$$

Because of the similarity of the reassociation and the carbonium ion–azide reaction, information on the mechanism is available from the product-ratio in various media and in the presence of added materials.

As in the previous paper, we assume that the carbonium ion produced as an intermediate lasts sufficiently long to be treated as a separate electrochemical entity, *i.e.*, possessing an ionic radius, solvation layer, ionic atmosphere, activity, etc. Accordingly the life of the carbonium ion must exceed $10^{-8}$—$10^{-10}$ sec., the time of building up of an ionic atmosphere.[3]



The potential energy curve of a competitive substitution is illustrated in the Figure. The lower curve represents the energetics of a unimolecular competitive substitution. After acquiring sufficient activation, the alkyl halide decomposes into the ions. The

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* Part I, preceding paper.

[1] Bateman, Hughes, and Ingold, *J. Amer. Chem. Soc.*, 1938, **60**, 3080.

[2] *Idem*, *J.*, 1940, 974.

[3] Harned and Owens, " Electrolytic Solutions," Reinhold Publ. Co., New York, 1950; Chap. IV.

solvation of the ions lowers their potential energy as shown by the valley which may be considered as an initial state of two reactions; each one in order to reach completion must pass an energy hill of different height. For comparison, the energetics of a bimolecular substitution is given by the upper curve. In a bimolecular competitive substitution two such curves must be drawn, which would differ along their entire lengths.

Hughes, Ingold, *et al.*[2,4] made a hypothesis that the carbonium ion–water reaction requires no activation because it occurs between the carbonium ion and one of the water molecules of the hydration shell surrounding the ion, simply by " collapse " of the shell. Thus if the water content exceeds the minimum necessary to build up a hydration shell, the water in the bulk of the solution no longer affects the rate of the carbonium–water reaction.

Our results do not support the " collapse " hypothesis. The relative amounts of products of competitive substitution of triphenyl- and diphenyl-methyl chloride are largely dependent on the water content of the solvent. The substitution products of di-*p*-tolylmethyl chloride are less sensitive to the solvent composition, but even there a trend is noticeable. Therefore we believe that the carbonium ion may react with any water molecule from the solution and not only with one of the hydration shell. Probably the particular molecule has to be activated in order to react.

The rates of reaction of the carbonium ion with an ion ($k_2'$) and a molecule (dipole) ($k_3$) are differently affected by the ionic-strength:

$$\log k_2 = \log k_2^0 + AI^{\frac{1}{2}}\,{}^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\log k_3 = \log k_3^0 + CI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $A$ and $C$ have the same meanings as in the preceding paper, and the index zero denotes zero ionic strength. The rate ratio of the two competing reactions at ionic strength $I$ is:

$$k_2/k_3 = (k_2/k_3)_0 \text{ antilog } (AI^{\frac{1}{2}} - CI) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since $A$ is negative, it is evident from eqn. (4) that this ratio decreases with increasing ionic strength.

In the case of a non-competitive hydrolysis of an alkyl halide, the ionic-strength effect slows the reassociation and thereby increases the overall hydrolysis rate. In a competitive substitution, the increasing ionic strength slows the carbonium ion–ion reaction (and also the reassociation) and thereby increases the share of alcohol in the products.

The rates of the two competing reactions are not sensitive in the same manner to the dielectric constant, $D$, whose effect on an ion–ion interaction is calculated by Scatchard.[5]

$$\log (k_2)_D = \log (k_2)_\infty - \frac{z_A z_B \mathbf{e}^2 \boldsymbol{N}}{2{\cdot}3\, D\boldsymbol{R}Tr_2^{\ddagger}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $r_2^{\ddagger}$ is the distance between the ions in the transition state, $(k_2)_\mathrm{D}$ and $(k_2)_\infty$ are the rates at $D$ and infinite dielectric constant respectively; $z_\mathrm{A}$ and $z_\mathrm{B}$ denote the charges of the ions. In the carbonium-ion–ion reaction $z_\mathrm{A}z_\mathrm{B} = -1$. Laidler and Eyring[6] calculated the effect of the dielectric constant on an ion–dipole interaction:

$$\log (k_3)_D = \log (k_3)_\infty + \frac{z^2 \mathbf{e}^2 \boldsymbol{N}}{2 \times 2{\cdot}3 D\boldsymbol{R}T}\left(\frac{1}{r} - \frac{1}{r_3^{\ddagger}}\right) \quad . \quad . \quad . \quad . \quad (6)$$

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* One should write $k_2'$ and $k_2'^0$, but the prime will be omitted for convenience and because of the similarity to the reassociation.

[4] Hawdon, Hughes, and Ingold, *J.*, 1952, 2499.
[5] Scatchard, *J. Amer. Chem. Soc.*, 1930, **52**, 52.
[6] Laidler and Eyring, *Ann. N.Y. Acad. Sci.*, 1940, **39**, 303.

where $r$ is the radius of the ion, $r_3^{\ddagger}$ is the distance between the ion and the centre of the dipole axis in the transition state.

Combination of eqns. (5) and (6) gives:

$$\left(\frac{k_2}{k_3}\right)_D = \left(\frac{k_2}{k_3}\right)_\infty \text{antilog}\left\{\frac{Ne^2}{2{\cdot}3DRT}\left(\frac{1}{r_2^{\ddagger}} - \frac{1}{2r} + \frac{1}{2r_3^{\ddagger}}\right)\right\} \quad . \quad . \quad . \quad (7)$$

According to equation (7), the rate ratio of the two competing reactions decreases with increasing dielectric constant. In the non-competitive hydrolysis of an alkyl halide, the increasing dielectric constant brings about a deceleration of the reassociation reaction (*i.e.*, $\alpha$ decreases), whereas in a competitive substitution it causes an increase of the rate of the carbonium ion–dipole reaction and consequently the proportion of alcohol in the products becomes higher.

It is difficult to exploit eqns. (4) and (7) quantitatively. Eqn. (4) is valid only at infinite dilutions and eqn. (7) requires the knowledge of interionic and ion–dipole distances which are so far very obscure. Usually plots of rates against the reciprocal of the dielectric constant are drawn to determine, by extrapolation to infinite dielectric constant, the factors containing the radii in eqn. (5) or (6).[7] Equation (7) applies to competitive substitution, which is more complicated because we deal with ratios of unmeasurably fast rates. Further, Scatchard's and Laidler and Eyring's equations treat a salt solution as a continuous dielectric which is not true for real concentrations.[8]

These restrictions being considered, eqns. (4) and (7) only help toward a better qualitative understanding of the course of competitive substitution reactions of alkyl halides in various media in the presence of salts.

## EXPERIMENTAL

*Materials.*—Di-*p*-tolylmethyl chloride, obtained by passing dry hydrogen chloride through an ethereal solution of the alcohol (prepared by reduction of commercial *pp*′-dimethylbenzophenone with lithium aluminium hydride) over calcium chloride,[2] had m. p. 43°. Diphenylmethyl chloride was prepared similarly. Dioxan was purified according to Beste and Hammett [9] by successive refluxing over sodium hydroxide and sodium. Sodium azide was recrystallized from aqueous alcohol.[10] Diphenylguanidine was recrystallized from aqueous acetone. For the preparation of triphenylmethyl chloride and acetone, see preceding paper.

*Analysis of Products.*—In the solvents used, all the alkyl halides react completely, yielding the alcohol and the alkyl azide or alkyl thiocyanate. Hydrochloric acid is developed in equivalent amounts to the alcohol. Thus the product ratio is calculated by:

$$[\mathrm{ROH}]/[\mathrm{RN_3}] = x/(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $x$ is the titre of the acid liberated in the competitive substitution and $a$ is the acid liberated by complete hydrolysis of the alkyl halide (*i.e.*, without addition of sodium azide or thiocyanate).

Hydrochloric acid in the presence of such a weak salt as $NaN_3$ or NaSCN behaves like a buffer and consequently no sharp change of colour is observed by titration with indicators. However, conductometric titration of the acid with a weak base gives very good results [11] even in the presence of highly conducting salts like $LiClO_4$ and $LiNO_3$. The weak base used as a titrant was 0·1N-diphenylguanidine [12] (p$K$ = 10) in 75% acetone–25% water. Conductances were measured with the apparatus in the preceding paper.

The alkyl halide, in acetone or dioxan, was brought to thermostat temperature. Aqueous sodium azide or thiocyanate with or without other salts added was introduced quickly with a syringe pipette into the well-stirred solution. After about ten half-times of reaction, the solution was diluted with 75% acetone to make up 100 ml. and the acid was titrated as above.

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[7] Amis and LaMer, *J. Amer. Chem. Soc.*, 1939, **61**, 905.

[8] Hasted, Ritson, and Collie, *J. Chem. Phys.*, 1948, **16**, 1.

[9] Beste and Hammett, *J. Amer. Chem. Soc.*, 1940, **62**, 2481.

[10] *Inorg. Synth.*, 1939, **1**, 80.

[11] Grunwald, Florida State Univ., Tallahassee, Fla., personal communication.

[12] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

Aqueous dioxan reaction mixtures were also diluted with aqueous acetone to yield better conductometric plots.

The alkyl thiocyanates are not very stable. Swain *et al.*[13] reported that triphenylmethyl thiocyanate decomposes in 75% acetone at 25° with $k = 7 \times 10^{-4}$ sec.$^{-1}$, so the corresponding half-time is about 17 min., which is rather short. Therefore sodium thiocyanate was used as a substituent, as follows. After 4—5 half-times of reaction of the corresponding alkyl halide, the solution was quenched with ice-cold aqueous acetone and titrated quickly. The alkyl chlorides react much faster than the thiocyanates, so only minute amounts of the latter decompose during the process. Nevertheless, the results with thiocyanate are not as accurate as those with azide. Rate constants of the decomposition of the diphenylmethyl chlorides were determined by Hughes, Ingold, and co-workers [2,14] and of triphenylmethyl chloride by us (preceding paper). Results are in Tables 1 and 2.

TABLE 1. *The percentage of alkyl azide in the products upon completed competitive substitution of* 0·05M-RCl *in aqueous acetone and aqueous dioxan at* 25°.

Row *a*: in presence of 0·05M-$NaN_3$; *b*: in presence of 0·05M-$NaN_3$ and 0·25M-$LiClO_4$; *c*: in presence of 0·05M-$NaN_3$ and 0·25M-$LiNO_3$. Di = dioxan, Ac = acetone.

| Solvent | | Di 87·5% | Di 75% | Ac 87·5% | Ac 75% | Ac 66·7% | Ac 50% |
|---|---|---|---|---|---|---|---|
| *D* | | 7·5 | 14 | 25 | 31·5 | 36·5 | 47 |
| $\mathrm{Ph_3C{\cdot}Cl}$ | *a* | 89·7 | 82·5 | 62 | 50 | 33 | — |
| | *b* | 86·7 | 59 | 57 | 30·5 | 12 | — |
| | *c* | 88 | 68·5 | 58·5 | 36·5 | 23·5 | — |
| | *a*/*b* | 1·03 | 1·40 | 1·09 | 1·64 | 2·75 | — |
| | *a*/*c* | 1·02 | 1·20 | 1·08 | 1·37 | 1·40 | — |
| $\mathrm{(CH_3{\cdot}C_6H_4)_2CH{\cdot}Cl}$ | *a* | 58 | 51 | 59 | 56·3 | 54·5 | 50 |
| | *b* | 44·5 | 40 | 50·7 | 47·5 | 44 | — |
| | *c* | 45 | 39 | 51·5 | 47·5 | 43·5 | — |
| | *a*/*b* | 1·30 | 1·27 | 1·16 | 1·18 | 1·24 | — |
| | *a*/*c* | 1·29 | 1·31 | 1·15 | 1·18 | 1·25 | — |
| $\mathrm{Ph_2CH{\cdot}Cl}$ | *a* | — | 22 | 24 | 15·5 | 12 | — |
| | *b* | — | 11 | 20·5 | 9·5 | — | — |
| | *c* | — | 12·5 | 19 | 9·5 | — | — |
| | *a*/*b* | — | 2·00 | 1·17 | 1·63 | — | — |
| | *a*/*c* | — | 1·76 | 1·26 | 1·63 | — | — |

TABLE 2. *The percentage of alkyl thiocyanate in the products.*

Conditions as stated in Table 1, except that NaSCN is present instead of $NaN_3$.

| Solvent | | Di 75% | Ac 87·5% | Ac 75% | Ac 66·7% |
|---|---|---|---|---|---|
| *D* | | 14 | 25 | 31·5 | 36·5 |
| $\mathrm{Ph_3C{\cdot}Cl}$ | *a* | — | 55 | 34·5 | 24·5 |
| | *b* | — | 51 | 32 | 21 |
| | *c* | — | 49·5 | 30·5 | 23·3 |
| | *a*/*b* | — | 1·08 | 1·08 | 1·17 |
| | *a*/*c* | — | 1·11 | 1·13 | 1·05 |
| $\mathrm{Ph_2CH{\cdot}Cl}$ | *a* | 31·5 | — | — | — |
| | *b* | 29 | — | — | — |
| | *c* | 29 | — | — | — |
| | *a*/*b* | 1·09 | — | — | — |
| | *a*/*c* | 1·09 | — | — | — |

## DISCUSSION

*Effect of Dielectric Constant on Competitive Substitution.*—According to eqn. (7), increase of the dielectric constant should decrease $k_2/k_3$ and yield a lower proportion of the alkyl azide. Table 1, row *a*, shows that triphenylmethyl chloride obeys this rule even when passing from one organic solvent to the other, whereas the diphenylmethyl chlorides obey it only within the same solvent. This may be due to the variation of the factor containing

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[13] Swain, Scott, and Lohmann, *J. Amer. Chem. Soc.*, 1953, **75**, 136.

[14] Hughes, Ingold, and Taher, *J.*, 1940, 949.

the radii when passing from one solvent to the other. The decrease of the amount of ditolylmethyl azide in the products with decreasing water content in acetone is well distinguishable, in contrast to the statement of Bateman, Hughes, and Ingold[2] (cf. p. 1335) relating to the "collapse" hypothesis. These authors analyzed the products by titrating the liberated acid with the aid of an indicator, but this method is rather insensitive for detection of the variations of the product ratio.

*Effect of Ionic Strength on Competitive Substitution.*—According to eqn. (4), an increase of ionic strength should decrease $k_2/k_3$ and yield a lower proportion of alkyl azide. This is confirmed in all experiments (Tables 1 and 2, rows *b* and *c*). The ionic strength was increased by addition of inert salts (lithium perchlorate and nitrate) in concentrations exceeding five-fold that of the reactants. These salts do not yield stable products with the alkyl halides used in aqueous solutions.[15] If alkyl perchlorates or nitrates were formed as intermediates during reaction, they would decompose rapidly to reproduce the same carbonium ion.

The constants *A* and *C* of eqn. (4) contain the dielectric constant in the denominator. Accordingly one would expect the effect of ionic strength to decrease with increasing water content in the solvent. Rows *a*/*b* and *a*/*c* indicate, however, that the contrary is true. Presumably this is to be attributed to the increasing degree of dissociation of the salts in solvents of higher water contents which causes a rise in the ionic strength. The fact that $LiClO_4$ usually produces a larger effect than $LiNO_3$ is probably also due to the higher degree of dissociation of the former (ref. 3, p. 564).

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[15] Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4861.