[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Rates of Alcoholyses of Triarylmethyl Chlorides

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Triarylmethyl chlorides react with alcohols to form ethers according to the reaction

$$Ar_3CCl + ROH \longrightarrow Ar_3COR + HCl$$

In this paper we present the results of a study of the relative reaction rates of some para-monosubstituted triphenylmethyl chlorides with ethyl alcohol in ether solution. We have also included measurements on the rates of alcoholysis of the related α-naphthyldiphenylmethyl chloride, β-naphthyldiphenylmethyl chloride and diphenylmethyl chloride. As we wished to study the possible changes which the I- and T-effects of the groups might produce in the reaction rate, we chose the para-substituted compounds, in which steric influences would be at a minimum.

We have also studied the kinetics of the reactions with respect to changes of the concentrations of the organic chlorides and of the reaction products but not with respect to changes of the concentration of alcohol. We have measured the heats of activation of all the reactions for which rate constants were obtained.

It was found that the rate of reaction of the key compound, triphenylmethyl chloride, with absolute ethyl alcohol was comparable with its rate of solution so ethyl ether was used as a solvent and a diluent. The reaction was found to proceed at a convenient rate in a mixture containing by volume at 25°, 60% ether and 40% absolute alcohol.

The reaction was followed by observing the rate of change of the electrical conductivity of a solution of the chloride, a method that could be used conveniently since the hydrochloric acid produced has a much higher conductivity than any of the other constituents. The hydrochloric acid concentrations were determined from conductivity–concentration curves constructed by measuring the conductivity of ether–alcohol solutions containing equivalent quantities of hydrochloric acid and triphenylmethylethyl ether in the concentration range 0.002 *N* to 0.00005 *N*. Such curves were constructed for each 5° interval between 0 and 30°, the results at round conductivities being read off and smoothed by difference curves. The concentration of organic chloride at any time was determined from the difference between the final hydrochloric acid concentration and the hydrochloric acid concentration at that time.

The alcoholysis of triphenylmethyl chloride was found to be complete at the concentrations used since the conductivity of a solution of hydrochloric acid was unchanged by the addition of an equivalent quantity of triphenylmethylethyl ether. The alcoholyses of the other trityl chlorides were also complete since the conductivities of their solutions in the alcohol–ether mixture finally reached that of a solution of hydrochloric acid containing the theoretical amount of the acid.

The reaction vessel consisted essentially of three parts, an alcohol chamber, a mixing chamber and a conductivity cell, and was so designed that the alcohol and the ether solution of the chloride could be brought to the bath temperature in the separate chambers, mixed, and then forced into the conductivity cell by external control. The temperatures of the thermostats used could be controlled to ±0.005°.

The conductivity cells contained parallel smooth platinum electrodes, 4 cm. in diameter and about 1 cm. apart. They were sealed in through the sides with platinum wire leads which connected to the bridge through mercury wells. They were designed following the recommendations of Morgan and Lammert[1] and conform to the specifications of Washburn[2] for the specific conductivity region measured. The cell constants were determined by measuring the conductivity of a 0.001 *N* potassium chloride solution.[3]

The usual Wheatstone bridge type of circuit was employed in measuring the resistance of a cell. A Leeds and Northrup type S. P. 929 bridge was used, the resistance of the cell being balanced against that of a L. and N. 99,990-ohm 4-dial resistance box by means of an L. and N. type 2470 (c) a. c. galvanometer, the deflections being observed through a wide angle lens. The galvanometer had a sensitivity of 0.025 microamp. per mm. scale division, a coil resistance of 1000 ohms and a period of three seconds; 110-volt, 60-cycle a. c. was used to activate the coils of the galvanometer and 6-volt, 60-cycle a. c. was used in the bridge circuit. During a run the galvanometer was employed as a null instrument, the time at which the bridge became balanced for a particular resistance being noted.

Preparation of Materials

(a) **Ethyl Alcohol.**—Commercial absolute alcohol was allowed to stand in contact with freshly broken pieces of lime for some weeks, in sealed bottles, then poured off and distilled from fresh lime through a vacuum-jacketed, packed, 3-meter fractionating column, the middle portion

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[1] Morgan and Lammert, THIS JOURNAL, **45**, 1692 (1923).

[2] Washburn, *ibid.*, **38**, 2438 (1916).

[3] "Int. Crit. Tables," Vol. VI.

being retained. This was redistilled from fresh lime, the middle portion, which boiled constantly to 0.01°, being retained. It was stored in bottles protected from the air by beakers paraffined over the top and withdrawn only by pressure of dry air through a pressure siphon: b. p. (corr.) 78.45°; $d^{25}{}_4$ (vac.) 0.78505; $n^{25}{}_D$ 1.35931.

(b) **Ethyl Ether.**—99.5% pure ether was dried with calcium chloride, then poured off and fractionated, the middle portion being retained and treated with sodium wire, fresh portions being added at intervals until it did not tarnish on standing for several days. This ether was then distilled from fresh sodium through the fractionating column, the middle portion boiling constantly to 0.01°, being collected. It was stored and transferred in a similar manner to the alcohol: b. p. (corr.) 34.45°; $d^{25}{}_4$ (vac.) 0.70792; $n^{25}{}_D$ 1.34919.

(c) **Triphenylmethyl Chloride.**—The Eastman product was recrystallized several times from a mixture of hexane and acetyl chloride, the product melting sharply and constantly at 113°. The maximum melting point in the literature is 112°.[4]

(d) **Triphenylmethyl Ethyl Ether. (Trityl Ether.)**—This was prepared by dissolving triphenylmethyl chloride in absolute alcohol and heating to get rid of hydrochloric acid. Upon cooling a 97% yield of the trityl ether separated, which after recrystallizing had a melting point of 83°; maximum melting point in the literature 83°.[5]

(e) ***p*-Halogen Derivatives.**—The four *p*-halogen derivatives were prepared by means of Friedel and Crafts reactions between benzophenone dichloride and the appropriate phenyl halide, following the method of Gomberg.[6]

Melting points, °C.		Maximum melting points in literature, °C.
p-I	122	123[7]
p-Br	114	114[8]
p-Cl	90	90[9]
p-F	87	Ref. 10

(f) ***p*-Tolyldiphenylmethyl Chloride.**—Prepared by means of a Friedel and Crafts synthesis using benzophenone dichloride and toluene; m. p. 100°; maximum m. p. in literature 99°.[9]

(g) **α-Naphthyldiphenylmethyl Chloride.**—The carbinol was prepared by means of a Grignard synthesis using benzophenone and α-naphthylmagnesium bromide.[11] The carbinol was converted into the chloride by saturating a hexane solution with dry hydrochloric acid in the presence of anhydrous calcium chloride; m. p. 169°; maximum m. p. in literature 169°.[12]

(h) **β-Naphthyldiphenylmethyl Chloride.**—The carbinol was prepared from ethyl-β-naphthioate and phenylmagnesium bromide. It was converted into the chloride in the usual manner; m. p. 93°; maximum m. p. in literature 94.5°.[13]

(i) ***p*-Anisyldiphenylmethyl Chloride.**—Prepared in the usual manner from Eastman *p*-anisyldiphenylmethylcarbinol; m. p. 123°; maximum m. p. in literature 123°.[14]

(j) ***p*-Nitrophenyldiphenylmethyl Chloride.**—Prepared from *p*-nitrobenzophenone dichloride and benzene by means of the Friedel and Crafts synthesis; m. p. 93°; maximum m. p. in literature 92–93°.[15]

(k) **Diphenylmethyl Chloride.**—Prepared in the usual manner from diphenylcarbinol. Purified by fractional vacuum distillation and fractional freezing; b. p. 156° (10 mm.); b. p. in literature, 167° (16 mm.); m. p. 14.5°; maximum m. p. in literature 17–18°.[16] Cl, 99.7% of theoretical.

The amounts of hydrochloric acid produced on alcoholysis of the trityl chlorides were measured by conductivity and found to be within 2% of the theoretical value in all cases.

Kinetics

When the logarithm of the concentration of the trityl chloride is plotted against elapsed time a straight line is obtained. This generalization was found to be true for every trityl chloride used and for the entire range in which measurements were made (95% or more completion). Two sample plots are shown in Fig. 1, in which ruled lines are shown passing through the experimental points. This shows that starting at any initial concentration the reaction is first order with respect to the trityl chloride and independent of the concentrations of hydrochloric acid and trityl ether.

The above kinetics show that alcoholate ion and hydrogen ion do not enter into the kinetics of the reaction in the range of hydrogen-ion concentration existing in our experiments, and that the reaction cannot be expressed by the scheme

$$\begin{gathered} \mathrm{RCl} \underset{\text{Fast}}{\rightleftharpoons} \mathrm{R}^+ + \mathrm{Cl}^- \\ \mathrm{R}^+ + \mathrm{R'OH} \underset{\text{Slow}}{\longrightarrow} \mathrm{ROR'} + \mathrm{H}^+ \end{gathered} \tag{1}$$

However, the schemes

$$\begin{gathered} \mathrm{RCl} \underset{\text{Slow}}{\rightleftharpoons} \mathrm{R}^+ + \mathrm{Cl}^- \\ \mathrm{R}^+ + \mathrm{R'OH} \underset{\text{Fast}}{\longrightarrow} \mathrm{ROR'} + \mathrm{H}^+ \end{gathered} \tag{2}$$

and

$$\mathrm{RCl} + \mathrm{R'OH} \longrightarrow \mathrm{ROR'} + \mathrm{H}^+ + \mathrm{Cl}^- \tag{3}$$

are permitted.

Scheme (3) represents all mechanisms in which the removal of chloride ion is assisted by the combination of an unshared electron pair of the alcohol, as for instance the formation of the transition

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(4) Gomberg, THIS JOURNAL, **24**, 618 (1902).

(5) Allan and Kolliker, *Ann.*, **227**, 114 (1885).

(6) Gomberg, *Ber.*, **37**, 1633 (1904).

(7) Gomberg and Cone, *ibid.*, **39**, 3279 (1906).

(8) Cone and Long, THIS JOURNAL, **28**, 520 (1906).

(9) Gomberg, *Ber.*, **40**, 1862 (1907).

(10) No mention of this compound was found in the literature. The equivalent weight, which was calculated from the amount of hydrochloric acid produced by alcoholysis as determined from the conductivity, differed from the theoretical value by only 0.05%.

(11) Gomberg, THIS JOURNAL, **36**, 1144 (1914); **41**, 1658 (1919).

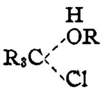
(12) Gomberg, *Ber.*, **37**, 1633 (1904).

(13) Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922).

(14) Gomberg, *ibid.*, **35**, 208 (1913).

(15) Baeyer and Villiger, *Ber.*, **37**, 606 (1904).

(16) Norris and Banta, THIS JOURNAL, **50**, 1807 (1928).

compound  $R_3C\begin{smallmatrix}H\\ \diagup OR\\ \diagdown Cl\end{smallmatrix}$ with absorption of energy followed by rapid loss of hydrochloric acid. Scheme (2) is kinetically identical with any mechanism in which the chloride ion is eliminated with the assistance of an unshared electron pair of the solvent, followed by a fast reaction to form the final products.

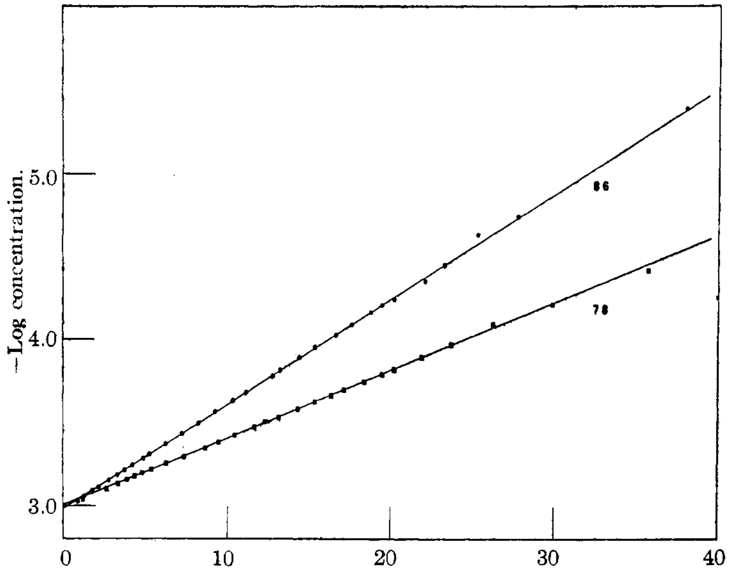


Fig. 1.—The alcoholysis of triphenylmethyl chloride at 0° (78) and at 5° (86).

Schemes (2) and (3) are equivalent to the S_{N1} and S_{N2} reaction types of Gleave, Hughes and Ingold.[17]

Scheme (2) implies a rate independent of the alcohol concentration, except in so far as any change in the composition of the medium changes the rate of ionization. Scheme (3) implies a bimolecular reaction. Since in our experiments the concentration of alcohol is large with respect to that of the trityl chloride, a pseudo-unimolecular reaction is observed.

When the proportion of alcohol to ether is increased the rate of the reaction is increased. But as the rate of the reaction is also increased by the replacement of ether by acetone, the increase of the rate of alcohol is consistent with either scheme (2) or scheme (3). In our experiments the solvent contains too much alcohol to enable us to distinguish between schemes (2) and (3). The increase of the rate with addition of acetone may be attributed to an increase in the polar character of the solvent. The English investigators consider that increase of rate with increase of polarity of solvent indicates an S_{N1} type of reaction. By itself it seems to be insufficient evidence to decide between the two types of reaction.

The values of the unimolecular or pseudo-unimolecular constants were obtained from the slopes of the lines in the plots of the logarithms of the concentrations of the trityl chlorides against time by multiplying by log *e* 10. The most probable slopes were obtained by Luten's method of averages.[18] This refinement is hardly necessary as the slopes obtained by inspection and those obtained by the method of averages rarely differed by as much as 1%. The values of the rate constants are given later in Table I. The rate of alcoholysis of triphenylmethyl chloride is about the same as that of acetyl chloride.

Dilution Effect.—It was found that when the initial concentration of trityl chloride was varied the first order rate constant increased as the initial concentration decreased. For triphenylmethyl chloride this effect is shown graphically in Fig. 2. The same phenomenon was found in the alcoholysis of every trityl chloride that was investigated at more than one initial concentration (see Table I). Since at every initial concentration the reaction is strictly first order, the value of the rate constant depends on the sum of the concentrations of trityl chloride and trityl ether. This was also shown in the following experiment. An experiment started with 0.00097 *M* triphenylmethyl chloride and 0.00093 *M* triphenylmethylethyl ether and its equivalent of hydrochloric acid gave a rate constant of 0.65 reciprocal minutes at 25°. The rate constant for 0.00097 *M* triphenylmethyl chloride is 0.76 but that for a concentration of triphenylmethyl chloride equal to the sum of the above concentrations of chloride and ether (0.00190) is 0.67, which is in close agreement with the value 0.65 found for the mixture.

When a definite velocity constant is obtained in any single run, but the value of the constant varies with the initial concentration, a factor affecting the rate is introduced with the reactants,

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[17] Gleave, Hughes and Ingold, *J. Chem. Soc.*, 236 (1935).

[18] Luten, *J. Phys. Chem.*, **39** 199 (1935).

and this factor is not sensibly altered by the change of reactants to products. In our experiments the factor is introduced with the trityl chloride and it partially protects the chloride from alcoholysis. It could be a property of an impurity or of one of the groups of the trityl chloride. In view of the existence of the phenomenon with so many different trityl chlorides it is improbable that it arises from the inhibitory effect of an impurity. The extreme dilution at which the phenomenon is observed (our experiments cover the range from 0.002 to 0.0001 *M*) suggests that it arises from an inhibition of some chain mechanism by the triarylmethyl group.

The best explanation seems to be that the alcoholysis of a trityl chloride has a dual mechanism and that one of the mechanisms is similarly inhibited by the trityl chloride and its ether. If it is assumed that the inhibition is first order with respect to the concentration of triphenylmethyl groups, the velocity constant is represented as a function of the initial concentration by the expression $k = k_1 + k_2/(k_3 + c)$, in which k is the overall rate constant, c is the initial concentration, and k_1, k_2 and k_3 are constants. k_1 is the velocity constant of a mechanism independent of the initial concentration, and k_2/k_3 that of the other mechanism at zero concentration. If the two mechanisms have approximately the same heats of activation, the approximate expression for all temperatures and concentrations is $k/e^{-E/RT} = a + b/(k_3 + c)$, in which e is the base of the natural logarithms, E is the heat of activation, R is the gas constant, T is the absolute temperature, and a and b are constants. This expression holds for the alcoholysis of triphenylmethyl chloride, as can be seen in Fig. 2.

The agreement between the points obtained at 0° and those at 25° shown in Fig. 2 corresponds to an approximate equality of within 2000 cal. between the heats of activation of the two mechanisms.

Apart from any theory of the dilution effect, the relative change of the rate constant with the initial concentration is approximately the same at 0° as at 25° for triphenylmethyl chloride. This may be assumed to be general for the alcoholysis of the trityl chlorides. Experimentally the relative change of rate was found to be greater at 0° than at 25° as often as it was found to be less. The observed differences are no greater than possible experimental errors.

The Effects of Substituent Groups.—The first order rate constants in reciprocal minutes for the alcoholyses of the substances tested are shown for two temperatures and generally at two initial concentrations in Columns 3 and 5 of Table I. This table also shows the heats of activation of the reaction, and the logarithms of the probability factors in the Arrhenius equation, $k = Ze^{-E/RT}$.

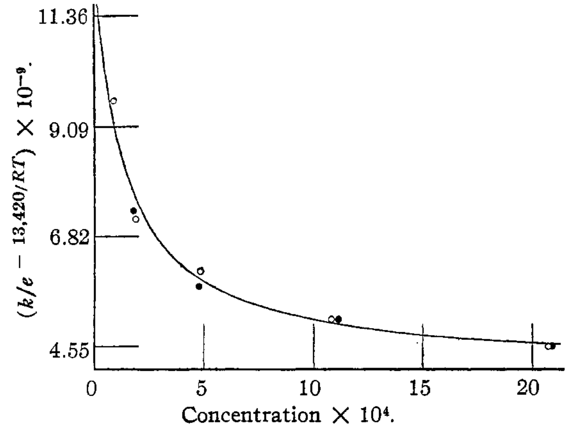

Fig. 2.—The effect of dilution upon the rate of alcoholysis of triphenylmethyl chloride. Open circles, 25°. Closed circles, 0°. The curve is $k/e^{-13,420/RT} = 4.09 \times 10^9 + (11.36 \times 10^9)/(1.4 + c \times 10^4)$. k is the observed first order rate constant and c is the concentration in moles per liter.

From the data in Table I we have constructed Table II, which shows the relative rates of the reactions. In this table, Column 2 shows the relative rates at 25° and at an initial concentration of 1×10^{-3} *M*. These are obtained by dividing the rate constant by that of triphenylmethyl chloride. Interpolation was used to obtain the rates at 1×10^{-3} *M*. Table II also contains in Column 4 the rate constants of the alcoholyses of some diphenylmethyl chlorides, divided by the rate constant of the alcoholysis of diphenylmethyl chloride. These figures are taken from the work of Norris and Banta.[19] The data of Columns 2 and 4 are placed in the same line when the substances are related in the same way to triphenylmethyl chloride and to diphenylmethyl chloride, respectively. Thus the rate of alcoholysis of *p*-tolyldiphenylmethyl chloride relative to that of triphenylmethyl chloride is in the same line as the rate of alcoholysis of *p*-tolylphenylmethyl chloride relative to that of diphenylmethyl chloride. The rate for benzyl chloride relative to that for diphenylmethyl chloride given in Column 4 is

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[19] Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).

TABLE I

REACTION RATES AND HEATS OF ACTIVATION

Concentrations are given in moles per liter and the pseudo-unimolecular specific rate constants, k_0 and k_{25}, are in reciprocal minutes. The values of log Z were calculated by use of the equation $\log Z = \log k + E/2.3RT$, in which k is the specific rate constant at 25° in reciprocal seconds, and R, E and T have their usual significance.

Methyl chloride	Concn. × 10^6 0°	k_0	Concn. × 10^6 25°	k_{25}	E	Log Z
Phenyl	...	...	9470	(2.5×10^{-8})	....	...
Diphenyl	1015 (30°)[a]	0.000120 (30°)[a]	1015	0.0000506	26,650	13.47
Triphenyl	1118	.0936	1088	.744	13,420	7.94
	478	.1062	481	.887	13,720	8.23
p-Methoxytriphenyl	915	(>9)	...	...	....	...
p-Tolyldiphenyl	973	.4312	1034 (10°)[b]	.958 (10°)[b]	12,450	7.82
	514	.5075	482 (10°)[b]	1.184 (10°)[b]	12,750	8.14
p-F-triphenyl	1118	.0691	1137	0.561	13,560	7.92
	520	.0846	531	.638	13,060	7.45
p-Cl-triphenyl	993	.0297	1018	.238	13,480	7.23
	478	.0340	497	.284	13,750	7.73
p-Br-triphenyl	1021	.0244	1004	.213	14,050	7.83
p-I-triphenyl	1051	.0327	1053	.251	13,190	7.30
	504	.0373	514	.293	13,350	7.48
p-NO_2-triphenyl	1032	.000614	1032	.00810	16,710	8.38
α-Naphthyldiphenyl	892	.1278	927	.9523	13,010	7.74
	432	.1672	458	1.233	12,940	7.81
β-Naphthyldiphenyl	1059	.1583	1091	1.180	13,010	7.84
	506	.1889	523	1.372	12,840	7.79
Acetyl chloride	1302	.1431	1320	0.994	12,550	7.43

[a] Too slow to be measured conveniently at 0°. [b] Too rapid to be measured conveniently at 25°.

TABLE II

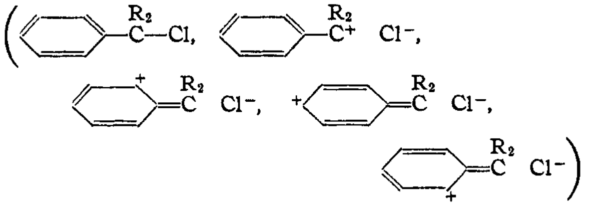
RELATIVE RATES OF ALCOHOLYSIS

Methyl chloride	Rate relative to triphenylmethyl chloride, 25°	Methyl chloride	Rate relative to diphenylmethyl chloride, 25°
p-CH_3O-triphenyl	(>90)	p-CH_3O-diphenyl	(1200)
p-CH_3-triphenyl	4.1	p-CH_3-diphenyl	16.2
Triphenyl	1.0	Diphenyl	1.0
p-F-triphenyl	0.76		
p-Cl-triphenyl	.32	p-Cl-diphenyl	0.42
p-Br-triphenyl	.28		
p-I-triphenyl	.34		
p-NO_2-triphenyl	.011		
β-Naphthyldiphenyl	1.59		
α-Naphthyldiphenyl	1.24	α-Naphthylphenyl	7.2
Diphenyl	0.00007	Phenyl	(0.002)
Phenyl	(.00000004)		

taken from our measurements and not from those of Norris and Banta.

As might be expected from the similarity of triphenylmethyl chloride and diphenylmethyl chloride, a close correlation exists in the effects of substituent groups on the alcoholysis rates of these substances. In every case cited in Table II, if the substitution of one group for another increases the rate of alcoholysis of a triarylmethyl chloride, it increases that of the corresponding diarylmethyl chloride. Any explanation of the effects of the groups on one of these types of reaction should be partially applicable to the other. However, the correlation is not perfect. The figures in Column 2 have no constant relationship to the co-linear figures of Column 4. One must conclude that no explanation of the effect of groups on the rates of alcoholysis of arylmethyl chlorides can be both simple and complete.

The effect of a substituent group on the rate of a reaction cannot be predicted without an assumption that, in the absence of complete knowledge of the mechanism of the reaction, is arbitrary. The arbitrary assumption that we shall make is that the high reactivities of arylmethyl chlorides are due to a molecular resonance involving aryl groups, and occurring chiefly in activated molecules; and that this resonance may be represented by the combination formula

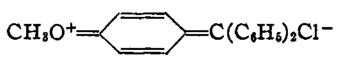


Substitutions that assist this resonance, either by increasing the number of resonating structures or by stabilizing positive charges on the ortho or para position, increase the rate of alcoholysis.

In di- and triarylmethyl chlorides all the aryl groups can in turn take on quinoidal structures and the resonance and reaction rates are greater the greater the number of aryl groups.

Any continuation of the conjugate system of a phenyl group by unsaturated groups in the ortho- or para-positions increases the number of possible resonating forms.

An atom having a pair of unshared electrons, and situated in the ortho or para position, introduces a new form in the resonance and increases the reactivity of the molecule. The effect of this new form will be very marked if the bonding power of the unshared electron pair is strong, for the new form is more stable than the other quinoidal forms as all of its atoms will have eight valence electrons. This type of group may be exemplified by the methoxy group. The additional form involved in the resonance of *p*-methoxytriphenylmethyl chloride has the structure



A chemically negative (—I) group is one that attracts negative electricity. Such a group in the para position reduces the stability of the quinoidal structure with a positive charge on the para carbon atom, reduces the resonance, and retards the reaction. A positive (+I) group has the reverse effect.

A group can have a tendency to retard the reaction because it is negative and at the same time have a tendency to assist the reaction because it introduces new forms into the resonance. A rigorous prediction is then impossible. However, in these cases it is often possible to see which of the opposing tendencies is predominant. For instance the chlorine atom and the methoxy groups are both negative, but both having unshared electrons in the requisite position can enhance the resonance. But as the negativity of the chlorine atom is much greater than that of the methoxy group, and the bonding power of its unshared electrons is less than that of the methoxy group, one may state with assurance that *p*-methoxytriphenylmethyl chloride reacts much faster than *p*-chlorotriphenylmethyl chloride. One may also expect, but not as a result of a rigorous analysis, that the negativity of the chlorine atom is its more important characteristic, and that the bonding power is the more important characteristic of the methoxy group, and hence that *p*-chlorotriphenylmethyl chloride reacts slower than, and *p*-methoxytriphenylmethyl chloride faster than, triphenylmethyl chloride.

The above discussion is well exemplified by the data shown in Table II. The triaryl compounds react much faster than the diaryl, which in turn react faster than the monaryl compounds. The positive (+I) methyl group produces high reactivity, while the strongly negative nitro group and halogen atoms produce slow reactions. The most strongly negative of these groups, the nitro group, produces the slowest reaction. The unshared pair of electrons of the methoxy group induces a very rapid reaction. The mono-naphthyldiphenyl derivatives are faster reacting than triphenylmethyl chloride, which is to be expected from the greater resonance associated with naphthyl than with phenyl groups. One should note, however, that the relative rates of the α- and β-naphthyl compounds are the reverse of that expected from their resonances. An α-naphthyl compound has one more quinoidal form than the corresponding β-compound. Nevertheless the β-naphthyldiphenylmethyl chloride reacts with alcohol faster than the corresponding α-compound.

The relative reactivities of the halogen compounds are interesting. Taking the relative strengths of the monohalogenoacetic acids as a measure of the relative negativities of the halogens, the decreasing order of negativities is fluorine, chlorine, bromine, iodine. The order of reactivities found in our experiments is a mixed order, fluorine, iodine, chlorine, bromine. This would suggest that the decreasing order of their resonance (+T) effects is fluorine, chlorine, bromine, iodine, which is such as to oppose the influence of their negativities.

The above suggested order of the T effects is the same as that of the strengths of the halogen bonds, but the reverse of the polarizabilities of the halogen atoms. It is the order proposed by Baddley and Bennett[20] to explain the effects of halogen substitution on the velocity of various reactions, and by Bettman, Branch and Yabroff[21] to explain the relative strengths of halogenophenylboric acids. It has been criticized by Robinson,[22] Shoppee,[23] and Baker,[24] who prefer the reverse order.

Heats of Activation.—The heat of activation of triphenylmethyl chloride was determined by measuring, in at least duplicate, the rate of alcoholysis at each 5° interval between 0 and 25°, inclusive. The logarithms of the average specific rate constants are shown plotted against the reciprocal of the absolute temperature in Fig. 3, the points falling on a straight line as required by the Arrhenius equation. The slope of this line when multiplied by 2.303 R gives the value of the heat of activation in calories per mole. The value of E so determined is 13,420 calories.

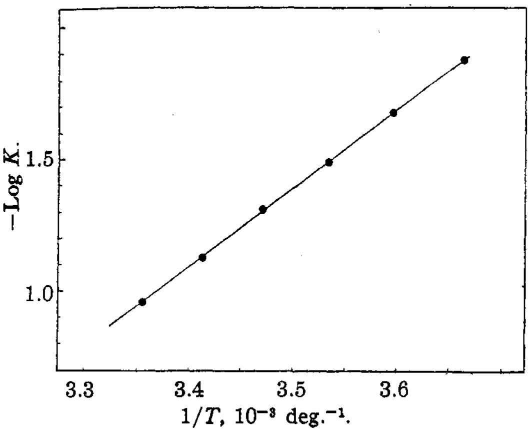


Fig. 3.—The variation of the rate of alcoholysis of triphenylmethyl chloride with temperature.

The values of the heats of activation for the other compounds studied were determined from the ratio of the rate constants at two different temperatures, usually 0 and 25°, and generally at two different concentrations. Table I gives the values of the heats of activation for all compounds for which rate constants could be determined at two different temperatures.

Generally speaking a rough correlation exists between rate and heat of activation: that is, the slower the absolute rate of a reaction, the larger is its heat of activation. This is especially noticeable in cases where a large difference in rate occurs as between di- and triphenylmethyl chlorides and p-nitrotrityl chloride and the other trityl chlorides. In the first case the difference in the heats of activation is more than sufficient to account for the observed difference in the rates, the Z factor for diphenylmethyl chloride being larger by a factor of 10^5 than that for triphenylmethyl chloride. The Z factors for the trityl chlorides are approximately equal, the variation in the rates depending chiefly on the variation of the heat of activation. However, with the exception of the p-nitro compound the differences in the rates are not sufficient to permit one to say unambiguously that this is the only factor which determines the rate.

The values of the heat of activation and Z factors found for the trityl chlorides are in the same general region as those usually associated with reactions between un-ionized molecules which produce an ionized product and belong to the class of reactions which are characterized by Moelwyn-Hughes[25] as "slow" reactions. The values of the calculated collision factors Z are less by a factor of about 10^4 than the value calculated from kinetic theory which is found to hold for the faster or "normal" reactions which are generally those between an un-ionized molecule and an ion. The value found for the alcoholysis of diphenylmethyl chloride is much closer to the calculated value, being about a power of ten greater. The values of E (26,500) and log Z (13.5) for this reaction are not considered to be as accurate as the others due to the slowness of the reaction and the fact that the rates were measured at temperatures only five degrees apart. They are probably accurate enough, however, to indicate that the differences between our values and those obtained by Norris and Morton,[26] namely, 21,200 calories for E and 11.23 for log Z, are real and due to the fact that they measured the reaction in 100% alcohol whereas we used the less polar solvent ether as a diluent.

Summary

The rates of alcoholysis of several triarylmethyl chlorides have been measured in a mixture of 60% ether and 40% alcohol by volume.

The kinetics of the reaction and the relative reactivities of the trityl chlorides are discussed.

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[26] Norris and Morton, THIS JOURNAL, **50**, 1800 (1928).