The Kinetics of the Ethanolysis Reaction of Some 4-Nitro-substituted Triphenylmethyl Chlorides

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The kinetics of the ethanolysis of three triphenylmethyl chlorides, the 4-nitro, 4,4'-dinitro, and 4,4',4''-trinitrophenylmethyl compounds, have been studied. The effect of change in substrate and solvent composition on the activation parameters, ΔH^{\pm} and ΔS^{\pm} , has been determined. For these

solvent composition on the activation parameters, ΔH^{\pm} and ΔS^{\pm} , has been determined. For these compounds, ΔH^{\pm} appears to be controlled by substrate structure while ΔS^{\pm} varies predominantly with solvent composition.

The attempted reaction of pyridine with 4,4',4''-trinitrophenylmethyl chloride to form the quaternary ammonium salt is also reported.

The reactions are interpreted to be proceeding via a carbonium ion-pair mechanism.

La cinétique de l'éthanolyse de trois chlorures de triphénylméthyl, le nitro-4, le dinitro-4,4' et le trinitro-4,4',4'' phénylméthyl, a été étudiée. L'effet causé par le changement du substrat et par la composition des solvants sur les paramètres d'activation, ΔH^{\pm} et ΔS^{\pm} , a été déterminé. Pour ces composés, il semble que le soit controlé par la structure du substrat alors que le ΔS^{\pm} varie essentiellement avec la composition du solvant.

La tentative pour réaliser la réaction entre la pyridine et le chlorure de trinitro-4,4',4'' phénylméthyl en vue de former le sel d'ammonium quaternaire est aussi relatée.

Un mécanisme impliquant une paire d'ions dont un ion carbonium est envisagé pour ces réactions. [Traduit par le journal]

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Introduction

Nucleophilic substitution reactions on the central carbon atom of triphenylmethyl chloride have attracted a number of investigators because of the relative stability of the derived carbonium ion under a variety of conditions (1). This compound reacts via a carbonium ion mechanism even under conditions adverse to the ionization process. Thus in a benzene solution, which is colorless, the second-order reactions observed are in fact bimolecular attacks of the reagent on the triphenylmethyl chloride carbonium ion-pair (2-11). In order to observe an S_N2 reaction the substrate molecule must have its ionizing capability reduced by electron-withdrawing substituents on the phenyl rings. Patai and Zabicki (12) studied the acetolysis of 4,4',4''-trinitrophenylmethyl chloride, but found no reaction in glacial acetic acid at 30 °C, although solvolysis took place in aqueous acetic acid via a carbonium ion mechanism. However, Miotti and Fava (13) investigated the radiochloride exchange in acetone solvent between the same substrate and tetraethylammonium radiochloride and presented evidence that the reaction was a direct $S_N 2$ attack on the covalent molecule.

In the present paper we report the rate constants and activation parameters for the 4nitro, the 4,4'-dinitro, and the 4,4',4''-trinitrotriphenylmethyl chloride undergoing ethanolysis in two solvents.

Results and Discussion

Ethanolysis Reaction

First-order rate constants were obtained for the ethanolysis of each of the substituted triphenylmethyl chlorides at a minimum of seven different temperatures over a 35-40° range. At most temperatures, three or four runs were made, although with the very slow reactions only two runs were carried out. Since the 4nitrotriphenylmethyl chloride was found to react with ethanol at about the same rate as it dissolves, the ethanolysis of this compound was measured in a solvent consisting of 30% v/v dioxane in ethanol. The 4,4'-dinitrotriphenylmethyl chloride was measured in both this mixed solvent and pure ethanol and the 4,4',4''-trinitrotriphenylmethyl chloride was studied only in ethanol. The results given in Table 1 were calculated by a least squares analysis of the data obtained by either the Guggenheim method (14) or from the

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Temperature (°C)	No. of runs	$10^4 k_1 (s^{-1})$	
(a) 4-Nitrotriphenylme	thyl chloride in 30% v/v	dioxane in ethanol	
-6.1	3	2.75 ± 0.08	
0.0	3	4.98 ± 0.15	
5.3	3	7.96 ± 0.04	
10.0	3	12.4 ± 0.06	
15.0	3	$3 19.2 \pm 0.06$	
20.0	3	3 29.5 ± 0.10	
25.0	3	44.5 ± 0.28	
29.9 ₅	3	63.3 ± 0.35	
(b) 4,4'-Dinitrotriphen	ylmethyl chloride in 30%	₀ v/v dioxane in ethanol	
29.9	3	0.339 ± 0.004	
40.0	3	0.855 ± 0.001	
45.0	3	1.263 ± 0.007	
50.0	3	2.039 ± 0.011	
55.0	3	3.005 ± 0.015	
60.0	3	4.403 ± 0.020	
65.0	3	6.476 ± 0.034	
(c) 4,4'-Dinitrotriphen	ylmethyl chloride in etho	anol	
20.0	2	0.845 ± 0.005	
24.9	4	1.476 ± 0.002	
30.0	3	2.47 ± 0.02	
35.0	4	3.91 ± 0.005	
40.0	4	6.33 ± 0.035	
45.0	3	9.69 ± 0.04	
50.0	3	14.79 ± 0.07	
55.0	3	22.24 ± 0.10	
(d) 4,4',4''-Trinitrotri	phenylmethyl chloride in	ethanol	
25.0	3	0.00432 ± 0.00001	
31.6	3	0.0103 ± 0.0001	
35.0	3	0.0148 ± 0.00002	
41.6	3	0.03135 ± 0.00014	
45.0	2	0.0444 ± 0.0003	
50.0	2	0.0746 ± 0.00003	
55.0	2	2 0.122 ± 0.001	
60.0	4	0.198 ± 0.001	
65.0	3	0.348 ± 0.001	

 TABLE 1. First-order rate constants for the ethanolysis of substituted triphenylmethyl chlorides

integrated first-order rate equation. The latter was used only for the runs which were too slow to follow over the three half-lives required by the Guggenheim method.

The rate constants of Table 1 were fitted to the transition state theory eq. 1 by a least squares computation. An example plot is shown

[1]
$$\log_{10}(k_1/T) = \log(k/h) + \Delta S^{*}/2.303R - \Delta H^{*}/2.303RT$$

in Fig. 1 from which it can be seen that, within the precision of the results there is no evidence of non-linearity in the dependence of $\log_{10}(k_1/T)$ on 1/T. The derived activation parameters are shown in Table 2.

Since there was no discernible temperature dependence of the enthalpy of activation, the heat capacity of activation, ΔC_p^{\dagger} seems to be indistinguishable from zero. This means it is less than about -30 cal deg⁻¹, which corresponds to a change of 0.1 kcal mol⁻¹ in ΔH^{\dagger} over a 30° temperature range.

The rate constants in Table 1 show that the order of solvolytic reactivity is trinitro < dinitro < mononitro derivative, which immediately suggests that we are dealing with a reaction, the mechanism of which involves an ionization as a rate determining step. This mechanism would be a classical S_N1 mechanism (15), which is at variance with the findings of Miotti and Fava

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Substituents:	4-Nitro	4,4'-Dinitro		4,4′,4′′-Trinitro
Solvent:	Dioxane/ethanol	Dioxane/ethanol	Ethanol	Ethanol
ΔH^{\pm} (kcal mol ⁻¹) ΔS^{\pm} (cal deg ⁻¹ mol ⁻¹)	$ \begin{array}{r} 13.5 \pm 0.1 \\ -23.9 \pm 0.2 \end{array} $	16.5 ± 0.1 -24.6 ± 0.3	17.1 ± 0.1 -18.6 ± 0.4	$20.1 \pm 0.2 \\ -17.2 \pm 0.5$

TABLE 2. Activation parameters for the ethanolysis of substituted triphenylmethyl chlorides



FIG. 1. Activation parameter plot for the solvolysis of 4,4'-dinitrotriphenylmethyl chloride in ethanol.

(13). However, the latter authors claimed a simple $S_N 2$ reaction only for the radiochloride exchange of the trinitro-derivative in acetone solvent. They noted that in acetonitrile solvent the first-order component of the reaction increased and the second-order component decreased. Nevertheless, in both solvents, both the first- and second-order rate constants were greater for the dinitro than for the trinitro compounds, *i.e.* the same order as we observe. To explain this the authors suggested that "bond breaking may well be predominant in these bimolecular substitutions". It is very difficult philosophically and experimentally to distinguish between a simple $S_N 2$ reaction with predominant bond breaking and a two-step mechanism with an ion-pair intermediate, although some erudite attempts have been made, particularly by Sneen

and coworkers (16-20) and by Scott (21). Sneen et al. have suggested that S_N reactions go via ion-pair mechanisms and that direct attack on the covalent substrate seldom, if ever, occurs. This postulate is based on a detailed analysis of only a few S_N reactions, although Scott (21) has expanded the scope of the theory by applying it to solvolysis reactions of primary alkyl compounds. Sneen's theory is analogous to saying that there are no covalent or ionic bonds in chemistry but only bonds intermediate between the two. For S_N reactions he has cut back the range for the pure S_N1 and S_N2 mechanisms to practically nothing, and increased the range for intermediate mechanisms and at the same time described the intermediate mechanisms in more concrete terms. This is the direction in which the study of reaction mechanisms ought to be going, but this does not necessarily mean that Sneen's description of S_N reactions is, at this time, more useful than Ingold's S_N1 and S_N2 . It seems clear that Miotti and Fava observed a reaction of trinitrotriphenylmethyl chloride in acetone, at least very close to a simple S_N^2 displacement, whereas it seems most likely that in the more polar ethanol solvents, the solvolysis reactions probably proceed through a carbonium ion-pair, i.e. the present results are consistent with Sneen's theory, although the solvolysis of this substrate molecule is not a rigorous test of the theory.

A comparison of the rates in the two solvents for the dinitro compound also shows that this substrate reacts about seven times faster in the more polar ethanol than in the less polar mixed solvent, again indicating that the transition state of the rate determining step has more charge separation than the initial state.

The activation parameters in Table 2 exhibit an interesting pattern in that the enthalpy of activation, ΔH^{\pm} , changes with substrate structure but not significantly with solvent change. On the other hand, the entropy of activation, ΔS^{\pm} , remains constant when the alkyl group is changed but is distinctly different for the two solvents.

The enthalpies of activation increase with

increasing number of nitro substituents, qualitatively as would be expected for a rate determining ionization step, since each strongly electron-attracting nitro group would make it more difficult for the electrons of the carbonchlorine bond to be transferred to the chlorine atom.

The fact that the entropies of activation do not change with substrate structure indicates. according to the criterion of Long and Schalager (22), that the mechanism of the reaction is the same for all three substrate molecules. However, the large negative values of ΔS^{\dagger} would classify these reactions on Long's criterion as S_N2, although Long set up the ΔS^{\dagger} test on the basis of hydrolysis reactions and cautioned that the complexity of the ΔS^{\dagger} parameter precluded a too quantitative use of its size as an indicator of mechanism. Since it can be seen that about -6cal $mol^{-1} deg^{-1}$ can be added to this parameter by the introduction of the non-reacting cosolvent dioxane, the ΔS^{\dagger} values cannot be considered evidence against an S_N1 mechanism but nevertheless may indicate non-typical behavior.

In a carbonium ion-pair mechanism either the first ionization step may be rate controlling $(S_N 1)$ or the second nucleophilic attack step may be rate controlling ($S_N 2 C^+$). For solvolysis reactions, in particular, intermediate mechanisms may be envisaged in which neither step is completely rate controlling. The mechanism for the ethanolysis of 4-nitro substituted triphenylmethyl chlorides is most probably an intermediate mechanism but well over towards $S_N I$, *i.e.* the ionization step to yield a carbonium ionpair is clearly the most important in controlling the rate but not necessarily exercising complete control. It is then easy to imagine that this mechanism changes to S_N2 with predominant bond breaking when the solvent is changed to acetone and the nucleophile to chloride ion, as found by Miotti and Fava (13).

Reaction of 4,4',4''-Trinitrophenylmethyl Chloride with Pvridine

Although the early literature contains many reports of the reaction of triphenylmethyl chloride itself with pyridine to form the quaternary ammonium salt, more recent work (4) shows that this reaction does not take place at atmospheric pressure, although Okamoto and Shimakawa (23) have prepared the salt at 4000– 5000 atm pressure. 4,4',4''-Trinitrotriphenylmethyl chloride $(10^{-3} M)$ in pyridine solution was maintained at 60–65 °C for 17 days, during which time the conductance of the solution increased by only a very small amount. If the quaternization reaction takes place it must be at least 500 times slower than the ethanolysis, or alternatively there is an equilibrium which overwhelmingly favors the reactants. Either of these alternatives is consistent with the proposition that an S_N2 reaction is not easily accomplished in the solvolysis of this type of substrate.

Experimental

4,4',4''-Trinitrotriphenylmethyl Chloride

This was prepared in a two-step process from triphenylmethane. The nitration was carried out according to the method of Shoesmith *et al.* (24) using a mixture of nitric and sulfuric acids at -5 to 0 °C. The nitrated methane was dried and recrystallized from chloroform – petroleum ether, m.p. 210–211 °C (lit. 212.5 °C (24)).

The chlorination of the trinitro derivative was carried out by the procedure given by Patai and Zabicky (12) using a similar apparatus. The reaction was carried out with 4 g of starting material and yielded 2.5 g of yellow crystals of 4,4',4''-trinitrotriphenylmethyl chloride, m.p. 199-204 °C (lit. 196-198 °C and 208 °C (12)). The n.m.r. spectrum (CDCl₃) gave δ 8.22, d, J = 9 Hz, 6H; 7.45, d, J = 9 Hz, 6H.

4,4'-Dinitrotriphenylmethyl Chloride

Ziegler and Mathes (25) described the preparation of this compound in 1930 using the method which Baeyer and Villiger (26) used for the preparation of 4-nitrotriphenylmethyl chloride in 1904 (see below). This method was found to work much more poorly for the dinitro derivative than for the mononitro derivation. Although on one attempt some product was obtained, it was not possible to purify it for kinetic measurements. The dinitro derivative was, therefore, prepared by the seven step procedure shown in Scheme 1.

Step 1. Diphenylmethane (75 g) was added in a fine stream to a vigorously stirred solution of nitric acid (390 g) and sulfuric acid (470 g) maintained at -10 to -20° . Stirring was continued for 45 min, the temperature not rising above -10 °C, then the solution was poured into an excess of ice water, the yellow precipitate filtered off, and washed with water, methanol, and hot diethyl ether. Yield of 4,4'-dinitrophenylmethane was 60 g, m.p. 186–189 °C (lit. 183 °C (27)).

Step 2. 4,4'-Dinitrophenylmethane (60 g) was dissolved in glacial acetic acid (700 ml) and the mixture refluxed. A solution of chromic anhydride (10 g) in water (110 ml) was slowly added through the top of the condenser and refluxing was continued for 2 h. The cooled solution was then added to an excess of ice-water, whereupon the crude 4,4'-dinitrobenzophenone precipitated. This was filtered, washed with water, NaHCO₃ solution, and water again, then dried at 90 °C. The i.r. spectrum contained a peak at 1675 cm⁻¹ (CHCl₃). The yield was 68 g, m.p. 183–186 °C (lit. m.p. 189 °C (27)).

Step 3. 4,4'-Dinitrobenzophenone (68 g) was added to 95% ethanol (500 ml), followed by NaBH₄ (3 g) and the

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Scheme 1

solution was allowed to stand 10 h, then poured into an excess of water. The yellow precipitate of 4,4'-dinitrodiphenylmethanol was collected and dried. The yield was 45 g, m.p. 160–162 °C. The i.r. spectrum showed a peak at 3570 cm⁻¹ (CHCl₃), but none at 1675 cm⁻¹.

Step 4. 4,4'-Dinitrodiphenylmethanol (45 g) was dissolved in dry benzene (700 ml). Freshly distilled thionyl chloride (59 g) was slowly added and the solution refluxed 8 h. The benzene and excess thionyl chloride were distilled off under reduced pressure leaving a brown oil. This oil was dissolved in a minimum quantity of hot benzene, and warm petroleum ether (90–120 °C) was added until the solution became cloudy. On allowing to stand overnight, yellow crystals formed. The yield of the 4,4'-dinitrodiphenylmethyl chloride was 30 g, m.p. 109– 111 °C. The i.r. spectrum showed no peak at 3570 cm⁻¹.

Step 5. 4,4'-Dinitrodiphenylmethyl chloride (30 g) was dissolved in dry benzene (800 ml). Freshly sublimed anhydrous aluminum chloride (30 g) was added slowly, and the solution refluxed for $3\frac{1}{2}$ h with vigorous stirring. On cooling, ice and dilute HCl were added to the stirred mixture. The whole mixture was poured into a separatory funnel and the aqueous layer drawn off. The benzene layer was washed twice with dilute HCl and the acid layers were collected and washed once with fresh benzene. The combined benzene layers were dried for at least 12 h over anhydrous CaCl₂, filtered, and the benzene was evaporated off at a rotary evaporator. The brown oil which remained was dissolved in the minimum quantity of benzene, and warm petroleum ether (b.p. 90-120 °C) was added until the solution became cloudy. Benzene was added to just clear the cloudiness and the mixture was allowed to cool slowly. After about 2 h, yellow crystals and a red oil formed. The residue was recrystallized several more times by the same procedure before a pure product, free from oily residue, could be separated. The yield of 4,4'-dinitrotriphenylmethane was 15 g, m.p. 160–165 °C.

Step 6. The methane (5 g) was dissolved in glacial acetic acid (150 ml) and heated under reflux, then a solution of chromic anhydride (7.5 g) dissolved in water (50 ml) was slowly added through the top of the condenser, after which refluxing was continued for 1 h. The reaction mixture was added to an excess of ice water, the yellow 4,4'-dinitrophenylmethanol which precipitated was collected, washed with water, NaHCO₃, and water again. The product was dried overnight, yield 4 g, m.p. 143–146 °C. The i.r. spectrum (CHCl₃) gave a peak at 3600 cm⁻¹.

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Step 7. The alcohol (4 g) was added to freshly distilled acetyl chloride (50 ml) and refluxed 12 h. Dry benzene (20 ml) was added and the excess acetyl chloride distilled off under reduced pressure. The volume of the benzene was reduced to about 10 ml on a rotary evaporator, and petroleum ether (b.p. 90–120 °C) was added until the solution became cloudy. On standing overnight yellow crystals of 4,4'-dinitrotriphenylmethyl chloride formed and were recrystallized from benzene – petroleum ether. The n.m.r. spectrum (CDCl₃) gave δ 7.2–7.5, m, 5H; 8.17, d, J = 9 Hz, 4H; 7.53, d, J = 9 Hz, 4H. The i.r. spectrum (CHCl₃) gave no peak at 3600 cm⁻¹. Potentiometric titration indicated 97% purity, by chloride analysis. The yield was 3.5 g, m.p. 139–140 °C (lit. m.p. 141 °C (25)).

4-Nitrotriphenylmethyl Chloride

This was prepared in a two-step reaction from nitrobenzophenone by the method of Baeyer and Villiger (26). The latter material was converted to 4-nitrobenzophenone dichloride using PCl₅. The product was crystallized from hot petroleum ether (90–120 °C). Yellow crystals were obtained, m.p. 54–55 °C (lit. 56–57 °C (26)). The dichloride was reacted with AlCl₃ in dry benzene. The crude product was recrystallized several times from hot petroleum ether (90–120°) before oil-free yellow crystals were obtained. Two final recrystallizations were made from petroleum ether in the presence of acetyl chloride. The

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FIG. 2. Run No. 192. Guggenheim plot for the solvolysis of 4,4'-dinitrotriphenylmethyl chloride in ethanol–dioxane (70:30 v/v) at 29.9 °C.



FIG. 3. Run No. 152. First-order plot for the solvolysis of 4,4',4''-trinitrotriphenylmethyl chloride in ethanol at 25.0 °C.

yield of the second step was about 4%, m.p. 90-92 °C (lit. 92-93 °C (26)). The n.m.r. spectrum (CDCl₃) gave δ 7.25-7.35, m, 10H; 8.15, d, J = 9 Hz, 2H; 7.47, d, J = 9 Hz, 2H.

Solvents

Ethanol was dried with Mg turnings and fractionally distilled. Dioxane was dried with anhydrous $CaCl_2$ for 24 h, then sodium metal for another 24 h, followed by 6 h refluxing over sodium metal. The dioxane was then fractionally distilled.

Kinetic Procedure

The rates were determined by following the change in conductance with time, using cells of ca. 25 ml capacity, shiny platinum electrodes, and cell constants of about

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0.01. The conductances were measured with a Wayne-Kerr bridge, type B221. The initial concentrations of the substrates were about 2×10^{-4} M or less and at such concentrations the relation between the produced HCl and measured conductance was found by experiment to be linear. Thus, most of the rate constants were calculated directly from the conductance readings using the Guggenheim method (14). However, the trinitro-derivative reacted too slowly below 50 °C to be followed over the minimum three half-lives, so the integrated first-order rate equation was used for these runs; the concentration of unreacted chloride being calculated from the HCl concentration read from a calibration plot. The calibration plots were set up using the precision burette described by Martin *et al.* (28). Two example runs are shown in Figs. 2 and 3.

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