139. *Tritylation and Detritylation of Active Methylene Compounds. Part III.*[1] *Kinetics and Mechanism of the Detritylation in Strongly Acid Media.*

By Saul Patai and Shlomo Dayagi.

The kinetics of several cleavage reactions of the type $Ph_3C{\cdot}CHX_2 + H^+ \longrightarrow Ph_3C^+ + CH_2X_2$ have been studied in acetic acid containing various amounts of sulphuric acid. The logarithms of the first-order rate coefficients are proportional to Hammett's acidity functions. The factors influencing the reaction rates are discussed and a mechanism involving a rate-determining unimolecular decomposition of the conjugate acid of the substrates is proposed.

In continuation of our previous investigation on the tritylation of active methylene compounds by triphenylmethanol[2] and by triphenylmethyl chloride[1] we have studied the kinetics and mechanism of these reactions. Preliminary experiments showed that the forward reaction, *i.e.*, the tritylation, could not be followed by any convenient kinetic method, because of both the slowness of the reaction and the considerable incursion of

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[1] Part II, preceding paper.

[2] Part I, *J.*, 1962, 716.

side reactions. On the other hand, it was found that the reaction is reversible and an equilibrium is reached, which at the acidities employed was generally nearer to the side of the starting materials: $Ph_3C^+ + CH_2X_2 \rightleftharpoons Ph_3C{\cdot}CHX_2 + H^+$, where X was methoxycarbonyl, ethoxycarbonyl, carbamoyl, or cyano. Accordingly we measured the kinetics of the reverse reaction, *i.e.*, of the detritylation, in order to determine the mechanism of this reaction and study the mechanism of the condensation.

RESULTS

The acid-catalysed cleavage of the central carbon–carbon bond of the substituted ethanes $Ph_3C{\cdot}CHX_2$ was followed spectrophotometrically by determining the amount of trityl ions formed at different times. The compounds studied were α-tritylmalonamide, ethyl and methyl tritylmalonate, and tritylmalononitrile. The cleavage of each compound was studied in acetic acid containing different amounts of sulphuric acid, at 30° and at 40°, except that the dinitrile was studied only at 30°. Each reaction was of the first order in the compound studied. Table 1 gives the first-order rate coefficients obtained in acetic acid containing 0·938 mole l.$^{-1}$ of sulphuric acid with widely varying concentrations of α-tritylmalonamide at 30°.

TABLE 1.

$[Ph_3C{\cdot}CH(CO{\cdot}NH_2)_2]$ (10^{-5} mole l.$^{-1}$)	1·56	3·12	3·64	5·2	10·3	15·6	20·8	26·0	52·0
10^4k_1 (sec.$^{-1}$)	1·555	1·556	1·525	1·590	1·568	1·565	1·541	1·550	1·600

TABLE 2.

First-order rate coefficients (k_1, in sec.$^{-1}$) of the cleavage of compounds $Ph_3C{\cdot}CHX_2$ in acetic acid in the presence of various amounts of sulphuric acid with the corresponding Hammett acidity function (H_0) values.*

Runs with $Ph_3C{\cdot}CH(CO{\cdot}NH_2)_2$.

$[H_2SO_4]$ (mole l._^{1})...	0·0469	0·0938	0·1877	0·3758	0·564	0·751	0·938	1·126	1·877
$-H_0$	1·325	1·575	1·892	2·305	2·520	2·710	2·835	2·955	3·350
10^5k_1, at 30°	1·051	2·35	3·325	6·38	9·32	12·3	15·53	19·2	34·0
10^5k_1, at 40°		5·05	7·95	16·27		31·0		49·3	77·8

Runs with $Ph_3C{\cdot}CH(CO_2Et)_2$.

$[H_2SO_4]$ (mole l.$^{-1}$)...	1·877	2·255	2·53	3·38	3·758	4·51	5·64
$-H_0$	3·35	3·55	3·66	4·06	4·24	4·60	5·06
10^6k_1, at 30°	0·975	1·609	2·60	6·56	11·16	24·5	97·5
10^6k_1, at 40°	3·91	6·15	10·2	25·5	37·8	99·0	347·0

Runs with $Ph_3C{\cdot}CH(CO_2Me)_2$.

$[H_2SO_4]$ (mole l.$^{-1}$)...	1·877	2·255	2·53	3·00	3·38	3·758	4·51	5·64
$-H_0$	3·35	3·55	3·66	3·90	4·06	4·24	4·60	5·06
10^6k_1, at 30°	0·558	0·959		2·58		6·10	18·6	70·3
10^6k_1, at 40°	2·48	3·87	6·36		16·94	24·0	64·0	226·0

Runs with $Ph_3C{\cdot}CH(CN)_2$.

$[H_2SO_4]$ (mole l.$^{-1}$)...	7·50	9·38	11·28	12·78
$-H_0$	5·92	6·76	7·55	8·14
10^6k_1, at 30°	1·935	7·89	66·5	286·0

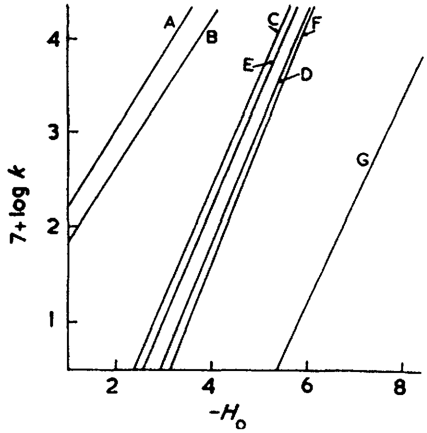
* Values of H_0 taken from the literature (Hall and Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487; Gold and Hawes, *J.*, 1951, 2102). The values at the highest acidities (11·28M- and 12·78M-H_2SO_4) were determined graphically from the curve extrapolated to the known value (−10·9) of H_0 in 100% H_2SO_4 (Brand, *J.*, 1950, 1002).

Each of the first-order rate coefficients given in Table 2 for the cleavage of the four compounds studied at various acidities is the average of 4—6 runs with different initial concentrations of the compounds, not differing from each other by more than ±2%.

Plots of log k_1 against the Hammett acidity function $-H_0$ of compounds $Ph_3C{\cdot}CHX_2$ gave good straight lines with slopes 0·74 and 0·72 for X = $CO{\cdot}NH_2$, 1·17 and 1·13 for X = CO_2Et, 1·20 and 1·12 for X = CO_2Me, at 30° and 40°, respectively, and 1·02 for X = CN at 30° (see Figure).

The energies and entropies of activation, calculated from the graphs at $H_0 = -4{\cdot}0$, were: 19·45 kcal. mole^{-1} and $-4{\cdot}3$ e.u. for X = $CO{\cdot}NH_2$; 24·8 kcal. mole^{-1} and $+2{\cdot}9$ e.u. for X = CO_2Et; and 25·4 kcal. mole^{-1} and $-0{\cdot}3$ e.u. for X = CO_2Me, respectively.

An attempt was made to determine the equilibrium constants, K_{eq} of the various reactions. Owing to the incursion of side reactions results were irreproducible. Only with α-tritylmalonamide, whose cleavage gave the fastest of the compounds studied, were more or less consistent results obtained at different acidities (see Table 3). In view of the extreme sensitivity of K_{eq} on the spectrophotometrically determined values of the concentration of trityl ions in the equilibrium mixture (see Experimental), the values in Table 3 may be considered satisfactory, with an average value of $K_{eq} \sim 1{\cdot}7 \times 10^{-3}$.



Plots of $-H_0$ against log k_1 for the cleavage reactions of:

A, B: $Ph_3C{\cdot}CH(CO{\cdot}NH_2)_2$ at 40° and 30°, respectively. C, D: $Ph_3C{\cdot}CH(CO_2Et)_2$ at 40° and 30°, respectively. E, F: $Ph_3C{\cdot}CH(CO_2Me)_2$ at 40° and 30°, respectively. G: $Ph_3C{\cdot}CH(CN)_2$ at 30°.

TABLE 3.

Average equilibrium constants, K_{eq}, of several determinations at various initial concentrations of $Ph_3C{\cdot}CH(CO{\cdot}NH_2)_2$ at each acidity; and the percentage of reaction (% of Ph_3C^+) of $4{\cdot}563 \times 10^{-5}$M-amide at various sulphuric acid concentrations.

$[H_2SO_4]$ (mole l.$^{-1}$)......	0·0469	0·0938	0·1877	0·3758	0·564	0·751	0·938
10^3K_{eq}	2·10	1·40	1·84	1·81	1·83	1·71	1·38
Ph_3C^+ (%)	74·4	77·1	89·3	94·0	95·7	96·5	96·6

DISCUSSION

The heterolysis of carbon–carbon single bonds has rather special requirements. In general, the cleaved molecule must have the tendency to produce one, or preferably two, ions of pronounced stability. Conrow[3] studied the cleavage of tropylidene derivatives of active methylene compounds in acids; Nesmeyanov *et al.*[4] investigated the cleavage of compounds of the type $(p\text{-}NMe_2{\cdot}C_6H_4)_3CR$, where R was $CH_2{\cdot}CHO$, $CHMe{\cdot}CHO$, $CH_2{\cdot}CH{:}CH{\cdot}CHO$, $CH_2{\cdot}CH{:}CH_2$ or $CHMe{\cdot}NO_2$, in both acid and neutral conditions; Holmberg[5] studied the cleavage of triarylmethylmalonate and of 5-triarylmethlybarbituric acids, and followed the kinetics of the reaction in aqueous ethanol at relatively high temperatures and pressures. In all these cases, as also in our examples, carbonium ions were produced as the primary products, generally simultaneously with an active methylene compound. The reaction is probably an attack by an electrophilic agent on the fragment of the molecule bearing electron-attracting groups.

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[3] Conrow, *J. Amer. Chem. Soc.*, 1959, **81**, 5461.

[4] Nesmeyanov, Perevalova, Volkomen, and Shalavina, *Izvest. Acad. Nauk S.S.S.R., Otdel. khim. Nauk.* 1951, 692; Nesmeyanov, Volkomen, and Perevalova, *ibid.*, p. 699; Nesmeyanov, Lavrushin, Shmaeva, and Perevalova, *ibid.*, 1956, 309.

[5] Holmberg, *Acta Acad. Aboensis, Math. Phys.*, 1949, **16**, No. 6; 1950, **17**, Nos. 1 and 3.

The dependence of the rate coefficients on Hammett's acidity function is a strong argument in favour of a mechanism involving a pre-equilibrium between the reacting molecule and a proton, followed by a unimolecular rate-determining decomposition of the protonated species.[6] The small absolute values of the entropies of activation (between —4·3 and +2·9 e.u.) are generally accepted as indicating that the transition state is similar to the initial state of the reacting molecule and not more ordered than the latter,[7] *i.e.*, that the rate-determining step is probably unimolecular. These conclusions are in accordance with the following reaction mechanism:

$$\mathrm{Ph_3C{\cdot}CHX_2 + H^+ \xrightleftharpoons{\text{Fast}} [Ph_3C{\cdot}CHX_2H]^+}$$

$$\mathrm{[Ph_3C{\cdot}CHX_2H]^+ \xrightleftharpoons{k_1} Ph_3C^+ + X{\cdot}CH{:}XH}$$

$$\mathrm{X{\cdot}CH{:}XH \xrightleftharpoons[\text{Fast}]{\text{Fast}} CH_2X_2}$$

The first step is a fast equilibration between the starting material and its conjugate acid, which in the second, slow and rate-determining, step gives the corresponding carbonium ion and the " enolic " form of the active methylene compound [$\mathrm{RO_2C{\cdot}CH{:}C(OH){\cdot}OR}$, $\mathrm{H_2N{\cdot}CO{\cdot}CH{:}C(OH){\cdot}NH_2}$, and $\mathrm{NC{\cdot}CH{:}C{:}NH}$, respectively]. This " enolic " form is in fast equilibrium with the corresponding active methylene compound. Participation of the enolic form has to be postulated in order to satisfy the principle of microscopic reversibility;[8] in the condensation the attack by electrophiles on active methylene compounds probably involves enolic forms of the latter, especially in strongly acid media.[9] The proposed mechanism, therefore, is also applicable to the reverse reaction, *i.e.*, to the condensations described in Parts I and II.[1,2]

The slopes of the plots of log k_1 against H_0 deviate somewhat from unity; the extent of these deviations can be interpreted as " salt effects,"[10] *i.e.*, the effect of electrolytes added to the solutions on the activity coefficients of the reacting species. Its size depends on the nature of the reacting species, and therefore the extent of the deviations from unity in the slopes may be due to the presence of different functional groups. Indeed the slopes for compounds of similar structures, such as ethyl and methyl tritylmalonate, are practically identical.

The tendency of the different substrates of the type $\mathrm{Ph_3C{\cdot}CHX_2}$ to undergo cleavage increases in the order $\mathrm{X = CO{\cdot}NH_2 > CO_2Et > CO_2Me > CN}$. This order is shown by the minimum amount of sulphuric acid needed in the reaction medium for the various substrates to undergo cleavage with measurable velocity, and also by comparison of the first-order rate coefficients for the reaction at constant acidity. The comparable rate coefficients for $H_0 = -4{\cdot}0$ at 30°, determined graphically from the plots of H_0 against log k_1, were $8{\cdot}75 \times 10^{-4}$, $4{\cdot}32 \times 10^{-6}$, $3{\cdot}73 \times 10^{-7}$, and $1{\cdot}69 \times 10^{-8}$ sec.$^{-1}$ for $\mathrm{X = CO{\cdot}NH_2}$, $\mathrm{CO_2Et}$, $\mathrm{CO_2Me}$, and CN, respectively. As these plotted lines are not exactly parallel, the relative magnitudes of the rates differ at various acidities, but their order remains the same throughout the range measured.

This order is the reverse of the order of reactivities of the corresponding methylene compounds in base-catalysed reactions[11] and it corresponds to the order of increasing

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[6] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791; Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[7] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 3574; Taft, Lee Purlee, Rietz, and DeFazio, *ibid.*, 1955, **77**, 1584; Long, Pritchard, and Stafford, *ibid.*, 1957, **79**, 2362.

[8] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1953, p. 216.

[9] (*a*) Hauser and Breslow, *J. Amer. Chem. Soc.*, 1940, **62**, 2389; (*b*) Noyce and Pryor, *ibid.*, 1955, **77**, 1397; (*c*) Noyce, Pryor, and Bottini, *ibid.*, p. 1402; (*d*) Noyce and Snyder, *ibid.*, 1958, **80**, 4024, 4034, 4324.

[10] McIntyre and Long, *J. Amer. Chem. Soc.*, 1954, **76**, 3240; Long and McIntyre, *ibid.*, p. 3243.

[11] Patai, Zabicky, and Israeli, *J.*, 1960, 2038.

basicity (*i.e.*, the tendency to undergo protonation) of the functional groups.[12] It seems therefore, that in the series of compounds studied, in which the cleavage is made thermodynamically possible by production of the same stable carbonium ion, the rate of the reaction is determined by the extent of protonation of the substrate, *i.e.*, by the equilibrium concentration of its conjugate acid in the various media.

EXPERIMENTAL

Materials.—Acetic acid, with a water content of less than 0·01%, was prepared from "AnalaR" glacial acetic acid.[13] Anhydrous sulphuric acid (m. p. 10·3—10·5°) was prepared according to Hall and Spengeman's directions.[14] Freshly prepared mixtures of acetic and sulphuric acid were used, in order to prevent the effect of "ageing."[15]

α-Tritylmalonamide and tritylmalononitrile were prepared as previously.[1,2] Methyl and ethyl tritylmalonate were prepared by the method of Lund *et al.*[16] The methyl ester was formed in 76% yield (m. p. 134°; lit.,[17] 130—131°), but we were unable to obtain it by Fosse's method.[17]

Kinetic Measurements.—The runs were followed in a Beckman DU spectrophotometer, in 1 cm. fused silica cells, in a thermostat-controlled cell compartment. The appearance of the absorption corresponding to trityl ions was followed at 406 mμ.[18] The molar absorption coefficient, ε, was determined by assuming 100% ionisation of triphenylmethanol in concentrated sulphuric acid and was found to be 36,900 (lit.,[18] 36,400). Actual concentrations of trityl ions were calculated according to Beer's law, which the solutions were found to obey. In the conditions of our experiments the optical density of solutions containing triphenylmethyl ions remained practically constant for several hours, showing that side reactions within the duration of the kinetic runs were negligible.

Some kinetic measurements were carried out in acidities in which un-ionised triphenylmethanol or its acetate may also be present.[18] In these cases, for calculation of the stoicheiometric concentration of the carbonium ions we used an arbitrary unit, ε′, the "apparent extinction coefficient" which was identified as $\varepsilon' = D/Cl$, *i.e.*, the value obtained by assuming that the observed optical density, D, corresponds to 100% ionisation of the product of concentration, C, at various acidities. At concentrations of sulphuric acid $>0{\cdot}75$ mole $l.^{-1}$ the values of ε and ε′ almost coincide.

The stoicheiometric amount of water even in carefully prepared sulphuric–acetic acid mixtures[18] is about 10^{-3} mole $l.^{-1}$, and the highest concentration of carbonium ions measured in our experiments was about 5×10^{-5} mole $l.^{-1}$. Hence the use of spectrophotometric results obtained from triphenylmethanol, with consideration of the equilibria involved, seems to be justified for our system, or at least cannot be the source of considerable error in the kinetic measurements.

Energies of activation were calculated from the Arrhenius equation.

Entropies of activation were calculated according to the absolute rate theory[19] by using the rate coefficient k' defined as $k' = k_1/h_0$ sec.$^{-1}$ mole^{-1}, where k_1 is the experimentally observed rate coefficient and h_0 is the antilog of $-H_0$.[9b]

Equilibrium constants K_{eq} were calculated from the equation

$$\begin{aligned} K_{eq} &= [Ph_3C^+]_{eq}[CH_2X_2]_{eq}/[Ph_3C{\cdot}CHX_2]_{eq}[H_2SO_4] \\ &= [Ph_3C^+]^2_{eq}/([Ph_3C{\cdot}CHX_2]_0 - [Ph_3C^+]_{eq})[H_2SO_4] \end{aligned}$$

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[12] Stewart and Yates, *J. Amer. Chem. Soc.*, 1960, **82**, 4059; Edward, Chang, Yates, and Stewart, *Canad. J. Chem.*, 1960, **38**, 1518.

[13] Griswold, Jones, and Birdwhistell, *J. Amer. Chem. Soc.*, 1953, **75**, 5701; Birdwhistell and Griswold, *ibid.*, 1955, **77**, 873.

[14] Hall and Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.

[15] Tolbert and Branch, *J. Amer. Chem. Soc.*, 1947, **69**, 1083.

[16] Lund, Hansen, and Voigt, *Kgl. danske Videnskab, Selskab, Mat.-fys. Medd.*, 1933, **12**, No. 9; Lund, *Ber.*, 1934, **67**, 936.

[17] Fosse, *Compt. rend.*, 1907, **145**, 1290.

[18] Gold and Hawes, *J.*, 1951, 2102.

[19] Wynne-Jones and Eyring, *J. Chem. Phys.*, 1935, **3**, 492; Glasstone, Laider, and Eyring, "Theory of Rate Processes," McGraw Hill Co., New York, 1941.

where the subscripts zero and eq correspond to the initial and equilibrium concentration, respectively. Substituting D_{eq}/ε' for $[Ph_3C^+]_{eq}$, we used the equation

$$K_{eq} = D^2_{eq}/\varepsilon'(\varepsilon'[Ph_3C{\cdot}CHX_2]_0 - D_{eq})[H_2SO_4].$$

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[*Received, August* 31*st*, 1961.]