

On the Reaction between the *N*-Bromotetramethylsuccinimide–Tetrabutylammonium Tetramethylsuccinimide Complex and C–H Acidic Compounds

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The reaction between the *N*-bromotetramethylsuccinimide–tetrabutylammonium tetramethylsuccinimide complex and C–H acidic compounds has been studied. The main pathway leads to substitution of the acidic C–H bonds at the substrate by tetramethylsuccinimido groups, as exemplified by the formation of tris(tetramethylsuccinimido)acetonitrile from acetonitrile.

The reaction with acetone is ca. 10^5 times faster than that with acetonitrile and displays a spectacular colour phenomenon: the initially colourless solution, after a reproducible and controllable induction period, suddenly becomes intensely purple, the absorbance maximum of which signals the end of the substitution process. Approximately in parallel with the colour development is the build-up and decay of an ESR signal (a 1:2:3:2:1 quintuplet). The position of the colour maximum can be used as a kinetic probe, the inverse of which has the dimensions of a first-order rate constant. Using this parameter, it has been established that the reaction is approximately first order in acetone, has a kinetic deuterium isotope effect of ca. 5, and has a rate-determining step involving attack of base upon the substrate. The reaction is autocatalytic with respect to the primary product, *N*-acetyl tetramethylsuccinimide (reaction order ca. 0.5), and is catalysed by a number of added bases, corresponding to conjugated acids of *pK* in the range 7–23.

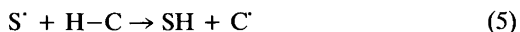
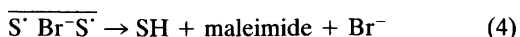
The mechanism most probably consists of an initial attack by tetramethylsuccinimide anion upon an acidic hydrogen of the substrate, followed by bromination of the enolate ion by the *N*-bromo imide. The bromo derivative reacts rapidly with tetramethylsuccinimide anion to give the substitution product. The purple colour and the ESR signal are due to species originating from further reactions of the primary products.

N-Bromo imides form molecular complexes with tetraalkylammonium salts of imides, as exemplified by the *N*-bromosuccinimide–tetrabutylammonium succinimide ($SBr/S^-Bu_4N^+$) complex.¹ This compound decomposes when allowed to stand in acetonitrile for 1 h at room temperature, giving succinimide (SH, ca. 65% yield) and polymaleimide (10–20% yield), the latter originating by base- and/or radical-catalysed polymerization

of initially formed maleimide.² The reaction exhibited weak chemiluminescence. *N*-Chlorosuccinimide and $S^-Bu_4N^+$ reacted in the same manner, although with a higher yield of polymaleimide (40%).

An electron-transfer (ET) mechanism was postulated for this transformation (eqns. 1–5), the key step being slow ET within the complex to form $SBr^{\cdot-}$ and S^{\cdot} , followed by very fast cleavage of the radical anion within the solvent cage to give bromide ion and a second S^{\cdot} . The two succin-

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imidyl radicals were assumed to undergo partial disproportionation, to yield SH and maleimide.^{2a} While this mechanism is reasonable in view of the undeniable radical characteristics of the process, it cannot be reconciled with the chemical properties exhibited by *S*⁻ in other types of reactions. The '*S*⁻' from eqn. (3) only gave products of hydrogen abstraction, either within the cage or from a solvent molecule after diffusion out of the cage, and none of the remaining reaction modes attributed to *S*⁻ (ring opening, attack upon aromatic rings, attack upon aliphatic double bonds; for reviews, see Ref. 3) could be verified experimentally. For some time, we avoided this problem by referring to the σ/π dichotomy³ and assigning the π structure to the *S*⁻ species, but later events⁴ eliminated this possibility.

One experiment designed to test the mechanism of eqns. (1)–(5) involved the decomposition of the *N*-bromotetramethylsuccinimide–tetrabutylammonium tetramethylsuccinimide complex (in the following to be abbreviated by $T_2Br^-Bu_4N^+$ or, less stringently, the '*T* complex') in acetonitrile. Since this complex lacks relatively easily abstractable α -hydrogens (the difference in C–H bond dissociation energy between tetramethylsuccinimide and succinimide is estimated to be 6 kcal mol⁻¹, using the C–H bonds in ethane and in the methylene group of ethyl methyl ketone as models) we anticipated that the disproportionation reaction of eqn. (4) would be blocked and the only product expected would then be tetramethylsuccinimide (TH). However, this experiment⁵ produced a totally unexpected product, tris(2,2,3,3-tetramethylsuccinimido)-acetonitrile (T_3C-CN), which, as detailed in the discussion, eventually led us to abandon the ET mechanism of eqns. (1)–(5) in favour of a more conventional polar one. This paper, together with a forthcoming one,⁶ is an account of the reactivity of $T_2Br^-Bu_4N^+$ toward acetonitrile and acetone and outlines a probable mechanism of

the rather complex set of phenomena accompanying the latter reaction. It has turned out that the loss of an interesting ET mechanism has been more than compensated for by the delightfully complicated and colourful phenomenology of the acetone reaction⁵ and indeed by many other reactions of the *T* complex with C–H acidic compounds.

Reaction of the *T* complex in acetonitrile

In contrast to the reaction of $SBr^-Bu_4N^+$ in acetonitrile, which takes place at 20.0°C on a time-scale of tens of minutes, the *T* complex required heating at elevated temperatures for long reaction times for reaction to occur. Reflux of the *T* complex (0.2 M) in acetonitrile for 45 h gave tetrabutylammonium bromide (100%), tetramethylsuccinimide (136%), *N*-butyltetramethylsuccinimide (2%), T_3CCN (22%) and a trace amount (<1%) of TCH_2CN .^{*} The presence of the latter compound indicated that it might be a precursor of the trisubstituted derivative, and this was substantiated by refluxing the *T* complex in benzene with authentic TCH_2CN as the substrate (1:1 ratio); this yielded 51% of T_3C-CN and 118% of TH. Phthalimidoacetonitrile, upon similar treatment with the *T* complex, gave phthalimidobis(tetramethylsuccinimido)acetonitrile (42%), accompanied by TH (130%).

The kinetics of the reaction of the *T* complex with acetonitrile was then followed at three temperatures, the progress of the reaction being

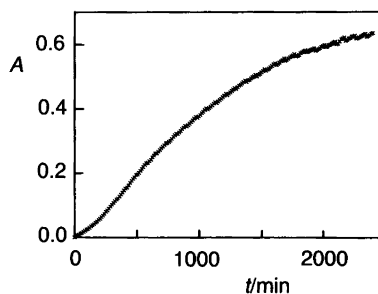


Fig. 1. Absorbance–time curve for the decomposition of the *T* complex (22.1 mM) in acetonitrile at 59.4°C.

*All yields were calculated on the basis of the following stoichiometry for replacement of one C–H bond by *T*: $T_2Br^- + C-H \rightarrow TH + Br^- + C-T$.

monitored by UV spectroscopy at 360 nm. A typical trace is shown in Fig. 1, and illustrates the short induction period. Omitting the first 10% of the reaction, first-order rate constants were calculated: at 59.4°C, $7.2(8) \times 10^{-4} \text{ min}^{-1}$, at 69.7°C, $2.3(3) \times 10^{-3} \text{ min}^{-1}$, and at 80.0°C, $6.8 \times 10^{-3} \text{ min}^{-1}$. An Arrhenius plot gave $E_a = 26 \text{ kcal mol}^{-1}$ (correlation coefficient = 0.9998).

In CD_3CN at 70.1°C, the reaction was considerably slower ($9.3 \times 10^{-4} \text{ min}^{-1}$ vs. $2.6 \times 10^{-3} \text{ min}^{-1}$ in CH_3CN), resulting in a kinetic isotope effect, k_H/k_D , of 2.8. This was the first indication that the mechanism of eqns. (1)–(5), involving a rate-determining intracomplex ET step, was not applicable to the reaction between the T complex and acetonitrile as such a step should not show any hydrogen isotope effect. It is also physically unrealistic to formulate a rate-determining step in which a T[•] abstracts a hydrogen atom from the solvent in the rate-determining step. Alternatively, a mechanism involving initial attack by base upon the substrate accounts adequately for the sizeable k_H/k_D . Additional and more compelling evidence in favour of such a step was obtained from a study of the reaction between the T complex and acetone and other C–H acidic compounds.

Reactions of the T complex in benzene

Before we continue with the acetone reaction, it is of relevance to report the outcome of the thermal decomposition of the complex in benzene. Still with the ET mechanism in mind, we hoped that any T[•] formed would only have one reaction mode, namely to attack benzene and give *N*-phenyltetramethylsuccinimide by analogy with the known reactivity of imidyl radicals.³ However, not even a trace of this product was detectable and instead TH (118%) and *N,N*-dibutyl-1,2-bis-(tetramethylsuccinimido)butylamine (11%), presumably formed by reaction of the T complex with tetrabutylammonium ion or subsequently formed tributylamine. Addition of an equimolar amount of tributylamine to a refluxing solution of the complex in benzene increased the yield to more than 60%.

Reaction of the T complex in neat acetone; phenomenology

At room temperature, the T complex dissolves in

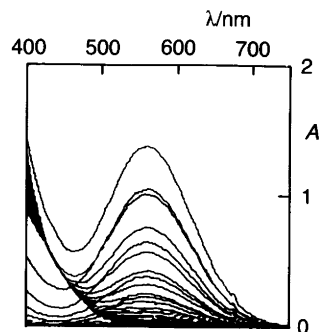


Fig. 2. UV spectra, taken at 5 s intervals, of a solution of the T complex (127 mM) in acetone at room temperature.

acetone to give a colourless solution. After 3–4 min, an initially 50–100 mM solution gradually assumes a purple colour (previously⁵ defined as 'blue', but 'purple' is more correct) which rapidly builds up to a maximum intensity (the solution becomes almost black in cm-thick layers) within less than a minute and then quickly fades away and is replaced by an orange–yellow colour which fades slowly to pale yellow (rate constant ca. 0.5 min^{-1}). When monitored by a rapid-scan UV spectrometer at 5 s intervals, the purple colour was seen to correspond to an absorption band with its maximum at 557 nm (Fig. 2). Monitoring the time dependence of the purple signal produced a trace of the type shown in Fig. 3.

The reaction exhibited weak chemiluminescence⁵ (solid line of Fig. 3), the intensity of which was proportional to $[\text{T complex}]^2$, as is also observed in the decomposition of the SBr/S^- com-

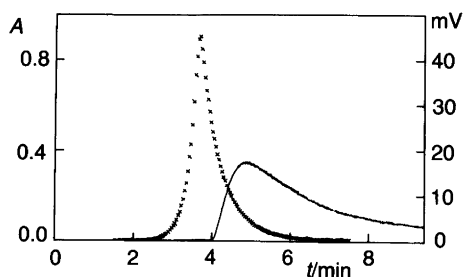


Fig. 3. Time dependence of the absorbance at 557 nm ($\times\times\times$; left ordinate axis) and the light emission (—) (measured as output in mV of the luminometer; right ordinate axis) of a 100 mM solution of the T complex in acetone at room temperature.

plex in acetonitrile. The decay of the light signal obeyed first-order kinetics with a rate constant of approximately 0.3 min^{-1} . We have not pursued the study of this chemiluminescence phenomenon further, since it is very weak and not easily ascribed to any particular series of molecular events.

The reaction products of a typical experiment were TH (119%), $\text{TCH}_2\text{COCH}_3$ (54%) and $\text{T}_2\text{CHCOCH}_3$ (28%), and other minor unidentified components. Starting with $\text{TCH}_2\text{COCH}_3$ and T complex in a 1:1 molar ratio in acetonitrile, the purple colour appeared 30 s after mixing and the reaction gave TH (110%), unchanged $\text{TCH}_2\text{COCH}_3$ (47%) and $\text{T}_2\text{CHCOCH}_3$ (58%, based upon unrecovered $\text{TCH}_2\text{COCH}_3$). A run in $(\text{CD}_3)_2\text{CO}$ gave TH (118%), $\text{TCH}_2\text{COCH}_3$ (59%) and $\text{T}_2\text{CHCOCH}_3$ (47%).

Since the reaction in neat acetone is typically over within 4–6 min, depending on the initial concentration of the T complex, it turned out to be technically difficult to determine the exact timing of all the various events connected with the reaction. In $(\text{CD}_3)_2\text{CO}$, a sizable kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} \approx 5$) reduced this problem and made possible a mapping of the reaction with respect to product formation ($\text{TCH}_2\text{COCH}_3$), development of the purple colour, the chemiluminescence signal and also to an ESR signal. The latter was a pentuplet with line intensities in the ratio 1:2:3:2:1, $\text{hfs} = 2.00$, $g = 2.00462$, indicat-

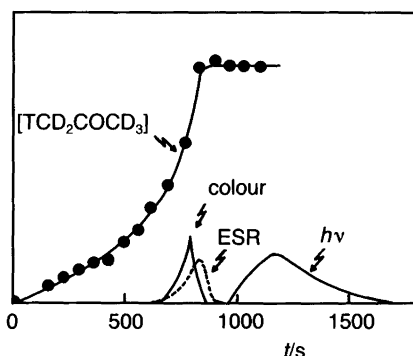


Fig. 4. Time dependence of the concentration of the monosubstitution product (monitored by NMR spectroscopy), the purple colour (UV, 557 nm), the light emission ($h\nu$) and the ESR signal, all on a relative scale, in solutions of the T complex in $(\text{CD}_3)_2\text{CO}$ at 23.8°C. Concentrations are in the order 170, 107, 137 and ca. 600 mM, respectively.

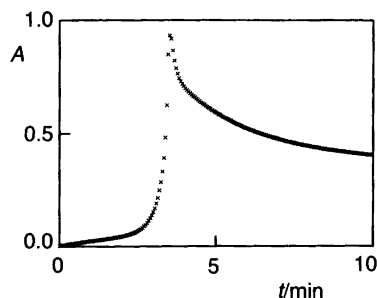


Fig. 5. Absorbance–time curve at 360 nm of a solution of the T complex (50.3 mM) in acetone at 20.0°C.

ing coupling of the unpaired electron to two identical nitrogen atoms. For the time being, we just note the appearance of the ESR signal and refer to a forthcoming paper⁶ for a more detailed account of this aspect of the reaction.

Fig. 4 shows the relative concentration profiles of $\text{TCH}_2\text{COCH}_3$ (as monitored by NMR spectroscopy, development of the signal of the ring methyl groups of the product at 1.19 ppm), the colour-forming species (UV), the radical (ESR) and the light-producing species during the reaction of the T complex in $(\text{CD}_3)_2\text{CO}$ at 23.8°C, the somewhat awkward temperature setting being determined by the temperature of the probe of the NMR instrument. The maximum concentration of the coloured species coincided almost exactly with the abrupt break in the product-formation curve. The latter has an unusual shape, strongly indicative of an autocatalytic process (see further below).

In acetone, the ESR signal was not detectable on the time-scale of the reaction period, ca. 5 min. It was, however, established that the break in the product-formation curve (monitored using the methylene signal of $\text{TCH}_2\text{COCH}_3$ at 4.24 ppm) again coincided almost exactly with the maximum of the purple colour (2.8 and 2.6 min, respectively, at 24.5°C).

Independent means of checking the unusual kinetic behaviour of the T complex in acetone were found in following the absorbance development at 360 nm (as done in the acetonitrile case). This curve is shown in Fig. 5, the maximum (4.17 min) of which agreed within the limits of error with that of the purple colour (4.06 min). More importantly, the course of the reaction could be followed by reaction calorimetry which

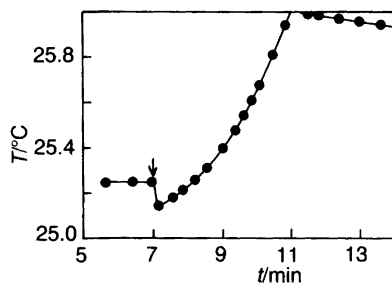


Fig. 6. Recording of a reaction calorimetric experiment, employing 0.16078 g of the T complex in 25.5 ml of acetone at 25.2°C. The reaction is started by crushing a glass ampoule containing the complex (at arrow). Initially, there is a small dip in the temperature owing to a negative heat of dissolution.

decisively demonstrated the autocatalytic nature of the reaction (Fig. 6). Again the time taken to reach the maximum of the purple colour almost coincided with the sharply defined end of the heat-producing period (3.5 and 3.8 min, respectively). The heat of reaction was calculated (two

experiments) to be 37.9(1) kcal mol⁻¹ at 25.1°C, the high value being expected for a reaction in which one equivalent of base is neutralized and a weak N-Br bond is replaced by a much stronger N-C bond.

Finally, it turned out that the change in the bias current during the ESR experiments provided an additional way of monitoring the progress of the reaction, again showing its autocatalytic nature (Ref. 6).

Kinetics of the reaction between acetone and the T complex

Since an autocatalytic reaction must necessarily be complex and thus difficult to analyse with respect to its kinetics, it occurred to us that the time taken to reach the absorbance maximum of the purple colour might be used as a useful kinetic parameter with which to characterize the reaction. It coincides quite well with the end of the product-formation period, is easy to measure, and, as shown below, is reproducible both in an

Table 1. Inter- and intra-batch reproducibility of the reaction of T₂Br⁻Bu₄N⁺ with acetone and the effect of water, using τ as a measure. All runs were carried out in acetonitrile (UVASOL®) at 20.0°C with [T complex]₀ = 107 ± 2 mM and [acetone] = 440 mM.

Batch No.	τ /min	<i>Int</i>	<i>A</i> _{max}	Remarks
I	46.0	1.82	0.35	
I	46.6	1.26	0.14	
I	46.4	1.42	0.24	
I	48.0	0.44	0.044	
I	46.8	3.04	0.38	
				Batch 1 (5 runs): Mean value of τ = 46.8(8) min
II	48.7	2.09	0.465	
II	47.9	1.98	0.414	
II	47.0	1.83	0.33	
II	47.4	1.74	0.345	
II	46.9	1.48	0.286	
II	46.2	3.00	0.498	
II	49.2	3.47	0.501	After pumping the sample for 30 min at 0.05 mmHg
II	47.6	3.11	0.492	After pumping the sample for 12 h at 0.05 mmHg
II	47.1	2.05	0.394	
				Batch II (9 runs): Mean value of τ = 47.6(9) min
II	47.9	18.8	1.67	Molecular sieves in cuvette
II	45.4	16.1	1.57	Molecular sieves in cuvette
II	46.7	1.05	0.214	Added [H ₂ O] = 3.6 mM
II	47.3	0.79	0.147	Added [H ₂ O] = 7.2 mM
II	46.7	0.52	0.088	Added [H ₂ O] = 14.4 mM
II	47.1	0.44	0.065	Added [H ₂ O] = 21.5 mM

absolute sense, i.e. within the same batch of complex and in a relative sense, i.e. between different batches of the complex. We denote the period to reach the maximum of the purple colour as τ /min; the inverse of this has the dimension time^{-1} and thus represents a rate constant.

Reproducibility. Within the same batch, τ was well reproducible as seen from Table 1, in which data are given for runs in both neat acetone and in acetonitrile (ca. 0.1 M in complex and 0.44 M in acetone) under standard conditions that were fixed to reduce the effect of a few experimental problems. Firstly, too short a reaction time gave mixing and thermal equilibration problems and consequently less precise measurements of τ , and secondly, the heat of reaction evolved over a short period of time such as that in neat acetone (3–4 min) produced a significant increase in temperature which, of course, affected the rate of the reaction. As an example, the temperature in a reacting solution of 42 mM of the complex in acetone, placed in the thermostatted cuvette holder of the spectrometer, increased by a maximum of ca. 0.9 K at the end of the reaction. This was noticeable in the form of a decrease in τ with increased concentration of the T complex ($\tau = 5.3$ min at 11.8 mM; $\tau = 3.8$ min at 92 mM).

Under the standard conditions in acetonitrile, τ was slightly less than 50 min (Table 1) and the effect of the heat evolved was small, at least when judged from the runs conducted at lower concen-

trations of the complex. During a run in a thermostatted cuvette with $[\text{complex}] = 0.1$ M and $[\text{acetone}] = 0.44$ M, there appeared a maximum temperature peak of 0.5 K* over a period (between 37 and 55 min) coinciding almost exactly with the period of the purple colour (between 35 and 50 min). The value of τ was independent of whether the reaction was carried out without any precautions having been taken to exclude air (normal way of operation) in making up solutions and running the reaction, or with oxygen bubbled through the solution before the run, or with argon protection during solution make-up and kinetic run. Nor did the presence of low concentrations of water affect τ at all (Table 1). On the other hand, water strongly influenced the intensity of the purple colour; at ca. 20 mM $[\text{H}_2\text{O}]$ it was still possible to record the position of the maximum with precision, but the absorbance maximum was reduced by a factor of ca. 10 (from 0.5 in a typical standard run with acetonitrile that had been stored over 3 Å molecular sieves to 0.06 in the wet acetonitrile).

Instead of the less precise recording of the absorbance maximum at 557 nm, all absorbance-time traces were integrated in order to give a measure of the total amount of the coloured species formed. This parameter (denoted *Int* in the

*When an identical run was performed without any efforts to keep the temperature constant, the temperature increase in the cuvette was ca. 2.5 K.

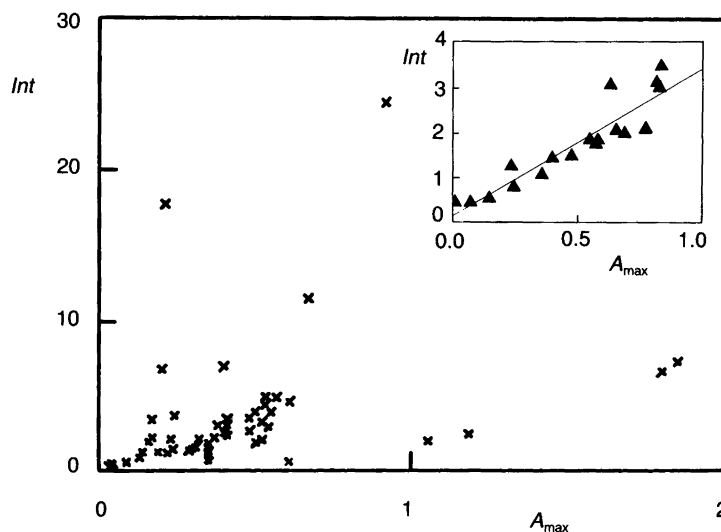


Fig. 7. Plot of *Int* vs. A_{max} under a variety of conditions. The insert shows *Int*– A_{max} variations under more strictly defined conditions (data from Table 1; all runs included except those with molecular sieves present).

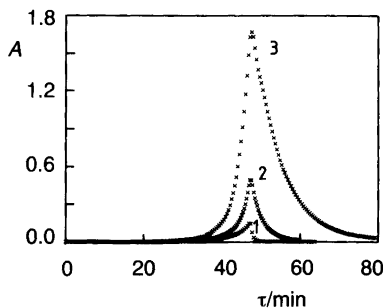


Fig. 8. Absorbance–time plots of solutions of the T complex (107 mM) and acetone (440 mM) in acetonitrile at 20.0°C with (1) water (7.2 mM) added, (2) no special precautions taken to prevent access of atmospheric moisture during make-up of the solution, and (3) molecular sieves present in the cuvette during the run.

following) does not correlate well with the maximum absorbance, A_{\max} (Fig. 7), unless one works within a series of strictly defined reaction conditions (see insert in Fig. 7). The reason for this behaviour is the difference in shapes of the absorbance–time curve under different conditions. The curves are relatively broad at longer reaction times, compared with those at shorter times. Int was, of course, equally as sensitive to the presence of water as A_{\max} (Fig. 8). Here the largest peak corresponds to a run in which molecular sieves were added to the solution in the cuvette before the reaction was started. This increased Int by a factor of more than 6 and A_{\max} by a factor of more than 3 with respect to the normal mode of operation.

Between different batches of the complex the reproducibility problem could be dealt with by normalizing all τ values with respect to the standard conditions for the solvent in question. This is illustrated in Table 2, which shows that comparisons between runs of different batches can be made without any serious errors being introduced. Interbatch comparisons have been avoided as much as possible, though, and most relationships derived in this paper were obtained from runs made using a single batch of complex.

The effect upon Int and A_{\max} is shown in Fig. 9, where they have been plotted versus $\log[H_2O]$. In general, water was not purposely added to the kinetic runs, and therefore both Int and A_{\max} values given here should be viewed with some reservation; since atmospheric water unavoidably

Table 2. Interbatch reproducibility of the reaction of $T_2Br^-Bu_4N^+$ with acetone, using relative values of τ as a measure. All runs were carried out in acetonitrile (UVASOL®) at 20.0°C with $[T\text{ complex}]_0 = 107 \pm 2$ mM.

[Acetone]/mM	Batch I, relative τ^a	Batch II, relative τ^b
440	1.00	1.00
113	0.33	0.31
223	0.57	0.56
853	1.75	1.68
1950	3.30	3.31

^aAbsolute value 46.8 min. ^bAbsolute value 47.6 min.

will enter the cuvette during the make up of the solutions and the sensitivity of Int and A_{\max} to variations in very low water concentrations (see for example Fig. 8, curve 2 under 'normal laboratory atmosphere conditions' and curve 3 with molecular sieves present in the cuvette) is extremely high, it was not deemed fruitful to standardize with respect to $[H_2O]$. With suitable calibration, it may well be that Int and/or A_{\max} could be developed into a sensitive probe of $[H_2O]$ at concentration levels below 0.1 mM.

The kinetics of the decay of the purple colour followed first-order behaviour, the three curves of Fig. 8 corresponding to k_{decay} of 0.134, 0.37 and 1.77 min^{-1} which is the order of increasing $[H_2O]$ in the reacting solutions. Even in the runs where $[H_2O]$ was known from weighing, there was no simple correlation between $\log(k_{\text{decay}})$ and $\log[H_2O]$, but it can at least be qualitatively concluded that water must somehow be involved in the reaction responsible for the bleaching process.

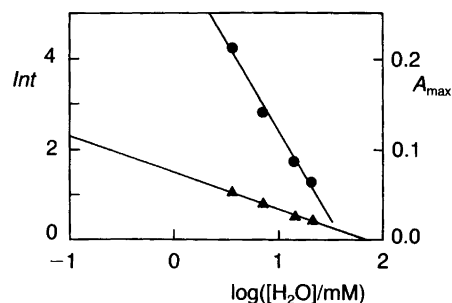


Fig. 9. Plot of Int (▲) and A_{\max} (●) vs. $\log([H_2O]/\text{mM})$.

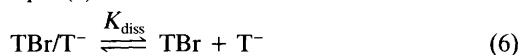
Table 3. Effect of added TBr or $\text{Bu}_4\text{N}^+\text{T}^-$ upon τ of the reaction between $\text{T}_2\text{Br}^-\text{Bu}_4\text{N}^+$ and acetone in neat acetone at 20.0°C and with $[\text{T complex}]_0 = 51 \pm 1$ mM.

Added [TBr]/mM	Added $[\text{Bu}_4\text{N}^+\text{S}^-]$ /mM	τ /min	$\tau^{-1}/10^{-2}$ /min ⁻¹	<i>Int</i>	<i>A</i> _{max}
2.0	—	5.1	19.6	0.66	0.47
2.9	—	7.3	13.7	0.67	0.53
3.7	—	9.7	10.3	0.70	0.47
4.7	—	11.4	88.8	0.71	0.45
7.7	—	19.4	5.15	0.72	0.45
10.7	—	29.3	3.41	0.76	0.46
14.4	—	37.9	2.64	0.92	0.38
18.0	—	56.6	1.77	0.92	0.43
22.6	—	75.5	1.32	0.83	0.43
—	3.0	2.5 ^a	40	0.57	0.55
—	3.9	2.3 ^a	43.4	0.50	0.52
—	9.3	1.3 ^a	76	0.41	0.53
—	17.2	1.1 ^a	91	0.38	—

^aThis τ value is presumably subject to a systematic error owing to the effect of the heat of reaction (which should give too low a τ value) and thus should only be semiquantitatively valid.

Dependence of τ upon excess TBr or T^- . Since the complex represents exact 1:1 proportions of T^- and TBr in the kinetic experiment – always a somewhat risky experimental situation – a series of experiments at various $[\text{TBr}]/[\text{T}^-]$ ratios was performed. These data (from runs in neat acetone) are given in Table 3 and partly in Fig. 10. The latter shows some of the features that have already been discussed above: with increased reaction times the absorbance–time curve becomes wider, whereas in this particular series of runs *A*_{max} does not change significantly. Note also the remarkable phenomenon of the colour appearance; the T complex + an additional amount of TBr was weighed in to give a colourless solution which after, e.g. 72 min (Fig. 10, curve 7) became faintly purple, almost black after 75.5 min and yellow after 80 min!

These data were analysed in terms of the simple assumption that the T complex dissociates into T^- and TBr, followed by a rate-determining attack by T^- upon acetone [eqns. (6) and (7)]. It is assumed that the rate constant with no extra TBr added to the solution is $(\tau^{-1})_0$, the dissociation constant of the complex is K_{diss} and the initial concentration of the T complex is C_0 . Then τ^{-1} with added TBr present can be expressed as in eqn. (8). The best fit of the data of Table 3 to



$$\tau^{-1} = (\tau^{-1})_0 \left\{ [(K_{\text{diss}} + [\text{TBr}])^2/4 + C_0 K_{\text{diss}}]^{1/2} - (K_{\text{diss}} + [\text{TBr}])/2 \right\} \quad (8)$$

eqn. (8) is shown in Fig. 11, with $(\tau^{-1})_0 = 13(2) \times 10^{-2}$ min⁻¹ and $K_{\text{diss}} = 8(2) \times 10^{-5}$ M. The fit is not ideal, presumably because of the possibility that TBr can tie up several T^- species at higher [TBr]; for complexes between *N*-bromo imides and bromide ion, it is known⁷ that 3:1 and 2:1 complexes exist. However, we did not deem it

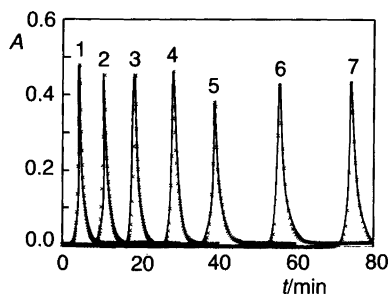


Fig. 10. Absorbance–time curves for solutions of the T complex (51 ± 1 mM) in neat acetone at 20.0°C, in the presence of added TBr, the concentrations of which are, in order from left to right, 2.0, 4.7, 7.7, 10.7, 14.4, 18.0 and 22.6 mM.

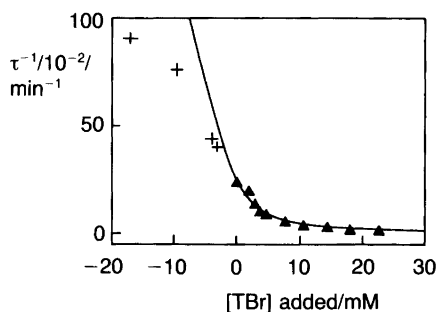


Fig. 11. Plot of τ^{-1} vs. [TBr] added under the conditions given in Table 3. The curve corresponds to the best fit of eqn. (8) to the experimental data (—); data used for the evaluation of the curve (\blacktriangle); experiments in which $T\text{-Bu}_4\text{N}^+$ was present in excess (+).

necessary to continue the analysis further on this point. Runs with added $\text{Bu}_4\text{N}^+\text{T}^-$ supported this assumption, in that τ^{-1} under these conditions was smaller than those calculated for the kinetic model of eqns. (8) and (7) (see Fig. 11).

Eqn. (8) also predicts that τ^{-1} should be proportional to $C_0^{1/2}$; this, however, was not the case. In runs in acetonitrile, τ^{-1} was essentially unchanged over a 215–13.6 mM range of C_0 . At the moment, we cannot account for this failure of the model.

The fact that $[\text{TBr}]/[\text{T}^-]$ strongly affects τ^{-1} easily explains the reproducibility problems between different batches of the T complex. Any slight difference in the required 1:1 ratio between the components during the preparation of the complex (see the Experimental) might be reflected in small deviations from the exact 1:1

Table 4. Effect of [acetone] upon relative τ^{-1} . The reactions were run in acetonitrile at 20.0°C at $[\text{T complex}]_0$ ca. 100 or 340 mM (last 4 runs). The five first values are the averages of those given in Table 2.

[Acetone]/mM	Rel. τ^{-1}
440	1.00
113	0.32
223	0.565
853	1.715
1950	3.305
170	0.428
340	0.776
679	1.46
1350	2.34

composition of the T complex. Around this point, the change in $\tau^{-1}/10^{-2}$ with a change of 1 mM in $[\text{T}^-]$ or $[\text{TBr}]$ is ca. 7 under standard conditions, which means that a change in the composition of the complex already at the 0.1% level will become detectable in τ^{-1} .

Effect of changes in acetone concentration and addition of $\text{TCH}_2\text{COCH}_3$. The runs listed in Table 4, conducted in acetonitrile at two levels of C_0 , concern the variation of τ^{-1} with the acetone concentration. A log/log plot of satisfactory appearance gave the order in [acetone] of 0.82(3).

The species predominantly responsible for the autocatalytic nature of the reaction was found to be $\text{TCH}_2\text{COCH}_3$ (Table 5 and Fig. 12). The kinetic order in $\text{TCH}_2\text{COCH}_3$ was determined in both neat $(\text{CD}_3)_2\text{CO}$ (0.55 ± 0.01) and in aceto-

Table 5. Effect of added $\text{TCH}_2\text{COCH}_3$ under different conditions. The reactions were run at 20.0°C at $[\text{T complex}]_0 \approx 51$ mM [in neat $(\text{CD}_3)_2\text{CO}$] or 108 mM (in acetonitrile).

Reaction conditions	$[\text{TCH}_2\text{COCH}_3]_0/\text{mM}$	$\tau^{-1}/\text{min}^{-1}$
$(\text{CD}_3)_2\text{CO}$, neat	0	3.36
$(\text{CD}_3)_2\text{CO}$	1.2	4.27
$(\text{CD}_3)_2\text{CO}$	2.4	5.46
$(\text{CD}_3)_2\text{CO}$	4.8	7.3
$(\text{CD}_3)_2\text{CO}$	9.4	11.5
$(\text{CD}_3)_2\text{CO}$	14.0	17.2
CH_3CN , no acetone added	4.3	10.4
CH_3CN , no acetone added	10.8	16.2
CH_3CN , no acetone added	42	38.3
CH_3CN , no acetone added	42	42.5

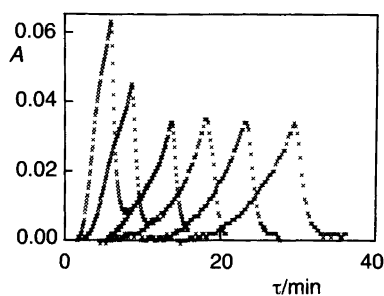


Fig. 12. Absorbance–time plots for solutions of the T complex in $(\text{CD}_3)_2\text{CO}$ under the conditions given in Table 5. $[\text{TCH}_2\text{COCH}_3]$ added is from left to right 14.0, 9.4, 4.8, 2.4, 1.2, and 0 mM.

nitrile, here without any acetone added (0.56 ± 0.01). In connection with the latter runs, it was found that the use of CD_3CN as the solvent did not significantly influence τ^{-1} .

With the assumption that attack of T^- upon acetone is the rate-determining step, it is logical to explain the autocatalytic effect of $\text{TCH}_2\text{COCH}_3$ as being due to general base catalysis by its carbanion. The $\text{p}K$ of $\text{TCH}_2\text{COCH}_3$ should be lower than that of acetone ($\text{p}K = 20$) and we have assumed here that it is similar to that of bromoacetone.⁸ A $\text{p}K$ value of 17 is then a

reasonable one. As the concentration of $\text{TCH}_2\text{COCH}_3$ builds up, the proton abstraction step becomes faster and faster and leads to the almost ‘explosive’ character of the reaction. A corollary of the hypothesis of general base catalysis would be to observe strong effects of other bases upon τ^{-1} , as was indeed also the case. When small concentrations (2–10 mM) of weak acids HA (in the $\text{p}K$ range 9–20) were added to standard runs, profound effects upon τ^{-1} were seen (Table 6), not to mention the equally strong colour effects that often were noticeable. As an example of the latter, indene (4.2 mM) added to a normal run (107 mM complex and 440 mM acetone in acetonitrile) caused the purple species to reach a maximum at 30.1 min followed by the appearance of a very strong green colour (absorbance ≥ 2.5 at 557 nm) at ca. 32 min. Only when the concentration of indene was reduced by a factor of 10 (0.42 mM) were the two maxima of approximately the same height (Fig. 13).

The $\text{p}K$ of tetramethylsuccinimide is 9.7,¹⁰ from which one can estimate $[\text{A}^-]_0$ in the cases listed in the Table. From this can be estimated the catalytic ‘rate constants’ for the various species added (Table 5). A Brønsted plot of $\log[(\tau^{-1})_{\text{cat}}]$ is given in Fig. 14; the β value comes out at 0.4(1).

It is worth noting that neither $\text{T}_2\text{CHCOCH}_3$, another product of the reaction, nor tetrabutyl-

Table 6. Effect of added weak acids upon $1/\tau$ of the reaction between the T complex (108 ± 2 mM) and acetone (440 mM) in acetonitrile at 20.0 °C.

Additive (concentration at $t = 0$ /mM)	$\text{p}K^{a,9}$	$\tau^{-1}/10^{-2}/\text{min}^{-1}$	$k_{\text{cat}}/\text{M}^{-1} \text{s}^{-1a}$
None		2.14	
2-Toluenethiol (3.0)	6.64	2.35	0.63
Nitroethane (2.9)	8.60	3.70	7.1
Acetylacetone (2.6)	9.02	6.54	23
DABCO (2.8)	9.7	2.54	2.7
Ethyl acetoacetate (2.5)	10.68	7.41	81
Malononitrile (3.6)	11.20	2.47	6.3
2,4,6-Tri- <i>t</i> -butylphenol (2.4)	11.70	2.86	29
Diethyl ethylmalonate (2.8)	15.0	2.87	1.1×10^3
$\text{TCH}_2\text{COCH}_3$ (3.3)	17 ^b	3.41	1.9×10^4
Indene (4.2)	18.5	3.32	8.4×10^4
Acetylacetone (5.5)	18.7	2.57	3.2×10^4
Phenylacetylene (10.1)	23.2	2.73	6.1×10^6

^aCalculated from the expression $(\tau^{-1})_{\text{add}} = (\tau^{-1})_0 + k_{\text{cat}}[\text{anion}]$, with the $\text{p}K$ of tetramethylsuccinimide taken to be 9.70 and K_{diss} for the T complex = $8 \times 10^{-5} \text{M}^{-1}$. ^bEstimated to be similar to that of bromoacetone ($\text{p}K = 17.5$).

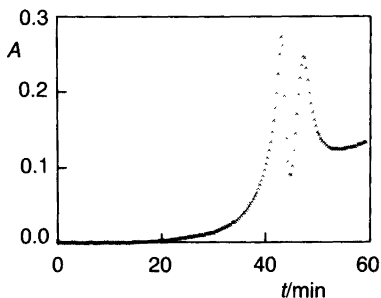


Fig. 13. Absorbance–time plot of a solution of the T complex (108 mM), acetone (440 mM) and indene (0.42 mM) in acetonitrile at 20.0°C.

ammonium bromide added in a concentration of 12.5 mM had any effect upon τ^{-1} . Also, no effect upon τ^{-1} was found on addition of tetramethylsuccinimide in concentrations of up to 100 mM, a somewhat unexpected finding in view of the ease by which homoconjugated anions¹¹ (of the general type $A-HA^-$) are formed in various systems. It would not have been surprising if the reactivity of T^- had been lowered by such an association, but now we need not consider the otherwise possible complication that TH, formed successively during the reaction, might influence the kinetics of the process.

The 1,3-disubstituted acetone, TCH_2COCH_2T , was conspicuously absent among the products of the T complex–acetone reaction. A sample was therefore prepared from Bu_4NT and 1,3-dichloroacetone and tested in its reaction with the T complex. Gratifyingly, the colour phenomenon and radical production turned out to be directly connected with this reaction; already at the 1 mM level of $[TCH_2COCH_2T]$ and with the T complex

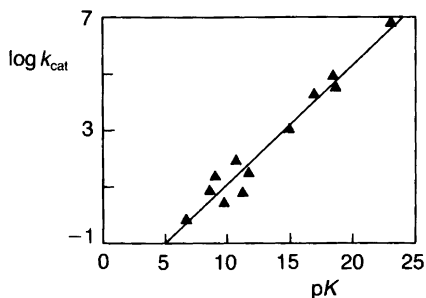


Fig. 14. Plot of $\log(k_{cat}/M^{-1} s^{-1})$ vs. pK of added weak acids (data from Table 6). The solid line of slope 0.42 represents the best fit to the data points.

present in the 2.5–100 mM concentration range, an acetonitrile solution developed an intense purple colour maximum within 1–3 min ($A_{max} \approx 2$, $Int \approx 30$) which decayed with a rate constant of the order of 0.15 min^{-1} . The ESR signal was a quintuplet of exactly the same appearance as that detected in the reaction between acetone and the T complex. These phenomena will be described in more detail in a forthcoming paper.⁶

Temperature dependence. Values of τ^{-1} were recorded at three temperatures (0.160 at 15.0°C, 0.211 at 20.0°C and 0.325 at 25.2°C, all in min^{-1}) in neat acetone and a value of $E_a = 11.5 \text{ kcal mol}^{-1}$ was obtained.

Test for possible radical character of the reaction. The possibility of a chain reaction involving T^- as the chain-carrying species is likely when mechanistic schemes for the reactions of the T complex are considered. Like *N*-bromosuccinimide,¹² TBr must be an ET oxidant with high reactivity* toward carbanions¹³ of the type that can be formed in the reaction between the T complex and C–H acidic compounds (see below). Since most compounds suitable for trapping radicals act as catalysts (Table 6) owing to the general base character of the corresponding anions, only a few meaningful experiments could be carried out along these lines. Dissolution of the complex in neat methyl methacrylate (distilled to remove inhibitor) or in the presence of acetone (1 M) in methyl methacrylate did not lead to polymerization of the monomer. The value of τ was not affected, under the conditions of a standard kinetic run in acetonitrile, by the presence of methyl methacrylate (72 mM), nor was it changed by adding 2-methyl-2-nitrosopropane (2.7 mM), a known inhibitor of radical chain reactions of the $S_{RN}1$ type.¹⁴

Reactions between the T complex and acetone in dichloromethane

A large number of kinetic experiments were also performed in dichloromethane, but these were

*Exploratory kinetic runs on the reaction between TBr and tris(4-methoxyphenyl)amine which produces the corresponding radical cation in a one-electron step,¹² showed that the ET reactivity of TBr is ca. twice that of *N*-bromosuccinimide.

much less informative owing to an important side reaction that took place between T^- and dichloromethane leading to the formation of T_2CH_2 ; the rate is comparable to that of the T complex-acetone reaction. This has the same effect upon τ as changing the $[TBr]/[T^-]$ ratio (see above), except that the change is less easily controlled. A certain amount of T^- is removed by reaction with dichloromethane, the $[TBr]/[T^-]$ ratio increases goes up, and τ increases exactly as shown in Fig. 10. Thus under our standard conditions ($[T \text{ complex}] = 107 \text{ mM}$, $[\text{acetone}] = 440 \text{ mM}$) τ in dichloromethane was 186 min as compared with 46.8 min in acetonitrile. Qualitatively, changing the variables in dichloromethane produced the same responses as in acetonitrile. Some of the data in dichloromethane are shown in Table 7.

Reaction between the T complex and other C-H acidic compounds

The T complex reacted with other C-H active compounds to produce substitution products of the same type as with acetonitrile and acetone, and some results of principal interest are included here. In order to obtain evidence for the first steps of the reaction sequence leading to the bromo substituted derivative, phenylacetylene (1.37 M) was allowed to react with the T complex (0.32 M) in acetonitrile at room temperature. After ca. 5 min, 1-bromo-2-phenylacetylene was formed in 78 % yield, which then underwent slow subsequent reactions with Bu_4NT over the next 20 h. In a separate experiment, 1-bromo-2-phenylacetylene was allowed to react with Bu_4NT in acetonitrile under similar conditions to give

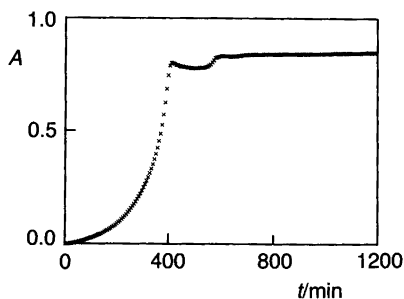


Fig. 15. Absorbance-time curve at 450 nm for the reaction of the T complex (62 mM) with cyclohexanone (312 mM) in dichloromethane at 20.0°C.

phenylacetylene (70 %, showing that the hydrogen/bromine exchange process is reversible), recovered bromophenylacetylene (20 %), 1-phenyl-2-(tetramethylsuccinimido)acetylene (5 %), 2-(tetramethylsuccinimido)styrene (7 %) and 1,2-dibromo-2-(tetramethylsuccinimido)styrene (74 %).

Cyclohexanone (neat) reacted rapidly with the T complex and began to develop a purple colour after only 20 s; this was immediately replaced by a much stronger red-brown colour (Fig. 15). Again the reaction was autocatalytic, and again the products were of substitution type. The main substitution product from the reaction between neat cyclohexanone and the T complex (0.1 M) at room temperature was 2-(tetramethylsuccinimido)cyclohexanone (14 %). The low yield could be explained on the basis of further reactions of the primary product, resulting in a complex mixture of elimination, oxidation and dimeric products.

4-Nitrotoluene ($pK = 20.5^{15}$) reacted readily

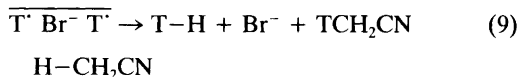
Table 7. Values of τ for reactions between the T complex and acetone (440 mM) in dichloromethane at 20.0°C.

[Complex] ₀ /mM	τ /min	<i>Int</i>	Remarks
10.4	300	0.026	
20.0	257	0.22	
30.9	225	0.35	
54.2	199	1.58	
108	168	2.75	
209	137	3.42	
107	75.4	1.77	3.1 mM in nitroethane
111	118	2.31	2.5 mM in 2,4,6-tri-t-butylphenol
108	160	2.26	2.2 mM in 2-propanol

with the T complex in benzene, acetonitrile and carbon tetrachloride to give *N*-(4-nitrophenyl)tetramethylsuccinimide in 54, 49 and 49% yield, respectively, together with TH (146–156% yield). In contrast, only a trace amount (<1%) of *N*-benzyltetramethylsuccinimide was obtained from toluene itself ($pK = 41.2$), the major product being the same as that formed in the reaction of the T complex and tetrabutylammonium ion/tributylamine.

Discussion

The reaction between the T complex and acetonitrile, forming products of tetramethylsuccinimido substitution into the C–H bonds of acetonitrile, with the tris-substituted product T_3CCN by far the predominating species, immediately raises difficult questions with regard to the intracomplex ET mechanism of eqns. (1)–(5): if such a substitution can take place by successive H atom abstraction and coupling by two T^\cdot radicals confined to a solvent cage at one of the ‘cage wall’ solvent molecules [eqn. (9)], why should the successive substitution products accumulate

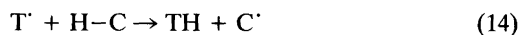
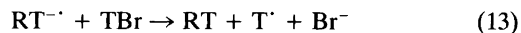
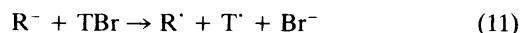


around the cage walls so as to drastically increase the chances of tris-substitution? If cage reactions are not involved, would T^\cdot be sufficiently selective to distinguish between acetonitrile and TCH_2CN to favour further reaction of the latter, in spite of the high $[CH_3CN]/[TCH_2CN]$ ratio, $\geq 10^3$ under the prevailing reaction conditions? And how can a kinetic deuterium isotope effect be explained, if ET within the complex is rate determining?

These problems, in combination with the unexpected phenomenology of the acetone reaction, especially that the reaction rate can be estimated to be ca. 10^5 times larger in acetone than in acetonitrile, led us instead to consider mechanisms in which base attack by T^- upon the substrate would be the rate-determining step. This would explain the high rate ratio (pK of acetone = 20 vs. 31 for that of acetonitrile), the kinetic deuterium isotope effect and the strong effect of small amounts of added weak acids. If such an assumption is accepted, two principally differing

mechanisms must be considered. They are both based upon the assumption that the T complex is kinetically inert and thus only serves as a source of T^- and TBr . This postulate is, of course, open to discussion, but we think that the bonding situation in the complex strongly diminishes its basicity as compared with T^- . In all probability the bonding between the two T units is of the $N\cdots Br\cdots N$ type, with the two formally negative nitrogens engaged in bonding to Br^+ and thus unable to act as external base centers. We intend to shed light upon this question by an X-ray crystallographic study of the T complex.

A mechanism that has many merits is the radical chain mechanism of eqns. (10)–(14), of similar type as the $S_{RN}1$ mechanism,¹⁶ in which the carbanion formed in the rate-determining step is oxidized in a one-electron step by $T-Br$, fol-

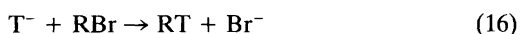


lowed by attack of T^\cdot upon a second carbanion to give the radical anion of the product. Chain transfer then occurs by reaction between the radical anion and a new TBr , etc. Termination would occur predominantly via hydrogen-atom abstraction by T^\cdot from a solvent C–H bond. Being a stronger acid than RH , the product RT would give rise to a larger carbanion concentration and hence increase the likelihood of the initiation step (11) occurring, resulting in an autocatalytic chain reaction. Moreover, the transient purple colour and the ESR signal in the acetone reaction might be ascribed to a radical anion appearing along the main reaction path, e.g. that of $T_2CHCOCH_3$.

Evidence discussed in more detail in a forthcoming paper,⁶ however, refutes this appealing mechanism. The purple colour does not correspond to a radical species and the radical detected appears *maximally* at the 10^{-6} M level. The potentials necessary to reduce reasonable candidates to form radical anions are so negative that it is unrealistic to postulate that such radical

anions would be formed in this system. A simple kinetic argument also rules out step (12): even in neat acetone, the enolate ion concentration in the presence of 0.1 M T⁻ is <10⁻⁵ M whereas the concentration of T[•], a highly reactive radical, must be several powers of ten lower. Hence any bimolecular reaction between R⁻ and T[•] should be very slow also if the rate constant is diffusion-controlled (10¹⁰ M⁻¹ s⁻¹). Finally, experimental evidence, albeit negative, does not favour a radical chain mechanism.

The polar mechanism of eqns. (10), followed by (15) (this step may be reversible, as indicated by the phenylacetylene results) and (16) removes



the kinetic constraints associated with reactions between species at very low concentrations. Here the carbanion reacts with TBr in an X-philic step,¹⁷ as shown from the reaction of *N*-bromosuccinimide with carbanions and carbanion equivalents,¹⁸ and the reaction between *N*-halo imides and halide ions,⁷ to produce RBr which then reacts in an S_N2 fashion with T⁻, the latter being in ample supply from the dissociation of the T complex. The first substitution product is a stronger acid than the starting material, thus giving rise to a higher concentration of a carbanion which in addition is a more efficient base for the initial step (10). This explains the strong autocatalysis and the effect of other weak bases in the acetone reaction. It is also reasonable to assume that further T-substitution occurs via base-catalysed bromination of the first substitution product, etc.

Some experiments for the verification of crucial steps of the polar mechanism have been performed. Bromoacetone reacts to completion within 30 s with Bu₄N⁺T⁻ in acetone at 20.0°C to give TCH₂COCH₃; 1,1-dibromoacetone similarly gives T₂CHCOCH₃ in the same way. In a more roundabout way, it was shown that TCH₂COCH₃ reacts with TBr in the presence of sodium hydride to give T₂CHCOCH₃.

The kinetic isotope effect of the acetone reaction, ca. 5, is in good agreement with other values for proton abstraction by bases from C–H acidic compounds where the difference in p*K* between

the substrate and the conjugate acid of the base (20–9.7 = 10.3) is ca. 10.¹⁹

Thus we end up with a rather conventional mechanism for the reactions of the T complex with C–H acidic compounds, at least along the pathway to the major products. However, the nature of the species responsible for the purple colour and the variables controlling its appearance are not obvious from this mechanism, nor is the formation of a well-behaved radical explained. We ascribe these phenomena to further reactions of the primary products. These reactions are of low abundance (maximally at the 1 mM level) but are excellently reproducible and presumably take place via electron-transfer mechanisms. These problems will be addressed in a forthcoming paper.⁶

A final comment on the mechanism proposed for the reactivity of the *N*-bromosuccinimide–succinimide anion complex, as outlined in eqns. (1)–(5), is in order. With the results from the T system in mind, a polar mechanism might apply also here: base-catalysed bromination of succinimide, followed by elimination of hydrogen bromide is certainly a reasonable mechanism leading to maleimide. In this connection it is pertinent to note that succinimide and/or *N*-bromosuccinimide in the presence of bromine in carbon tetrachloride can give rise to polymeric material, assumed to be polymaleimide.²⁰

Experimental

Methods. ¹H and ¹³C NMR spectra (in CDCl₃) were recorded on a Nicolet 300 MHz instrument, chemical shifts being given downfield with respect to SiMe₄. GLC–MS spectra were recorded on a Finnigan 4021 instrument at 70 eV, unless otherwise stated. Only the peak of the molecular ion and the most prominent peaks above *m/z* 155 (*M* of tetramethylsuccinimide) are given below. Elemental analyses were performed by the Microanalytical Laboratory of the Chemical Center or by Galbraith Laboratories, Inc., Knoxville, Tenn. USA.

Recordings of absorbance–time curves were performed as described earlier, using an Ultraspec spectrophotometer (LKB Instruments, Sweden) interfaced to an HP-85 microcomputer. The chemiluminescence measurements were made on a Luminometer 1250 (LKB-Wallac, Sweden).

The calorimetric measurements were made using an LKB-8721 reaction-solution calorimeter with a 25 ml glass vessel.²¹ The samples were placed in cylindrical glass ampoules (1 ml volume) with thin end-walls and narrow necks which were sealed under a low flame and detached. The measured enthalpy change was corrected for a small endothermal background effect due to the introduction of a small air bubble (ca. 1 ml) into the calorimeter liquid which results in some evaporation. Its magnitude was 0.088 cal.

Chemicals. Solvents used for kinetic measurements were as follows. Acetonitrile (p.a., UVA-SOL[®] from Merck, Darmstadt, FRG), stored over 3 Å molecular sieves, acetone (p.a., from May and Baker, Dagenham, UK), [²H₃]acetonitrile and [²H₆]acetone (from Ciba-Geigy, Switzerland) and dichloromethane (p.a., for residue analysis, Merck, Darmstadt, FRG). Other chemicals used were of the highest commercial quality available.

Preparation of tetrabutylammonium tetramethylsuccinimide. Tetrabutylammonium bromide (32.2 g, 0.1 mol) was dissolved in 300 ml of methanol (p.a., Merck) and silver(I) oxide (17.4 g, 0.075 mol) was then added in small portions with stirring. The mixture was stirred for 30 min (negative test for bromide ion with silver nitrate) and filtered through Celite onto tetramethylsuccinimide²² (15.5 g, 0.1 mol). After being washed with 2 × 100 ml of methanol, the filtrate was evaporated to give a viscous oil. Repeated additions and evaporations of toluene (2 × 100 ml) produced a crystalline mass of the salt which could either be used directly for further experimentation or recrystallized from toluene (150 ml) to give 25 g of the purified salt. ¹H NMR: δ 0.93 (t), 1.38 (m), 1.61 and 3.33 (2 × m, from Bu₄N⁺), 0.99 (s, from T⁻). ¹³C NMR: δ 13.7, 19.7, 24.0 and 58.6 (from Bu₄N⁺), 22.5 (CH₃), 48.6 (C) and 199.4 (CO) from T⁻. IR (0.025 M solution in acetonitrile): 1735 cm⁻¹ (weak). Anal. C₂₄H₄₈N₂O₄: C, H, N.

Preparation of the tetrabutylammonium tetramethylsuccinimide-N-bromotetramethylsuccinimide complex. The above procedure for the synthesis of the tetrabutylammonium tetramethylsuccinimide salt was carried out to the first evaporation stage, using 16.1 g (0.05 mol) of tetrabutylammo-

nium bromide. The oil was then dissolved in acetonitrile (200 ml) and a solution of N-bromotetramethylsuccinimide²² (11.7 g, 0.05 mol) in diethyl ether (100 ml) was added. Addition of diethyl ether (500 ml) and hexane (500 ml), followed by cooling in an ice-bath caused the T complex to crystallize, yield 27.0 g (86%), m.p. 157–160°C. The T complex could be recrystallized from acetonitrile–diethyl ether, m.p. 158–160°C. ¹H NMR: δ 0.94 (t), 1.28 (m), 1.67 (m), 3.36 (m) (from Bu₄N⁺), 1.00 (s, from T). ¹³C NMR: δ 13.9, 20.0, 24.2 and 58.6 (from Bu₄N⁺), 22.4 (CH₃), 48.0 (C) and 188.8 (CO) (from T). IR (0.025 M solution in acetonitrile): 1735 (very weak), 1655 cm⁻¹ (strong). Anal. C₃₂H₆₀BrN₂O₄: C, H, Br, N.

Preparation of N-cyanomethyltetramethylsuccinimide. Sodium (0.89 g, 0.039 mol) was dissolved in methanol (100 ml) and tetramethylsuccinimide (6.0 g, 0.039 mol) was added. After complete dissolution, the methanol was evaporated off to give a crystalline mass. Chloroacetonitrile (6.0 g, 0.080 mol) and N,N-dimethylformamide (DMF, 100 ml) were added and the mixture was refluxed with stirring for 1 h. The DMF was removed on a rotary evaporator and the residue treated with 500 ml of dichloromethane. The solid was filtered off and the solution was washed with water and dried with magnesium sulfate. Evaporation of the filtrate to dryness and recrystallization of the residue from toluene–hexane afforded 5.4 g (72% yield) of N-cyanomethyltetramethylsuccinimide, m.p. 75–76°C. ¹H NMR: δ 1.21 (s), 4.35 (s). ¹³C NMR: δ 21.3 (CH₃), 25.7 (CH₂), 47.3 (C), 113.2 (CN), 180.4 (CO). MS [*m/z* (%): 194 (*M*, 8), 179 (3). Anal. C₁₀H₁₄N₂O₂: C, H, N.

Preparation of N-acetyl tetramethylsuccinimide. This compound was prepared as for the cyanomethyl derivative from sodium (2.35 g, 0.102 mol) in methanol (250 ml), tetramethylsuccinimide (15.6 g, 0.1 mol) and chloroacetone (16.0 g, 0.17 mol) in 250 ml of DMF. Preliminary purification was by distillation, the main fraction (16.8 g) being collected at 118–122°C/0.2 mmHg. This product contained ca. 15% tetramethylsuccinimide which was removed by dissolution of the product in diethyl ether, followed by extraction with 0.025 M aqueous sodium hydroxide. After evaporation of the ether solution, final purification was effected by recrystallization from ethyl

acetate-hexane, m.p. 54–56°C. ^1H NMR: δ 1.19 (s, ring CH_3), 2.18 (s, CH_3), 4.24 (s, CH_2). ^{13}C NMR: δ 21.5 (ring CH_3), 27.1 (CH_3), 47.05 (CH_2), 47.1 (C), 182.2 (ring CO), 198.9 (CO). MS [m/z (%)]: 211 (M , 2), 169 (32). Anal. $\text{C}_{11}\text{H}_{17}\text{NO}_3$: C, H, N.

Preparation of 1,1-bis(tetramethylsuccinimido)-acetone. Sodium hydride (0.70 g, containing 20% paraffin oil, 0.023 mol) was washed with 2×20 ml of dry diethyl ether. Dry diethyl ether (50 ml) was then added, followed by 4.4 g of *N*-acetyl tetramethylsuccinimide (0.020 mol). The mixture was refluxed for 3 h, after which time *N*-bromotetramethylsuccinimide (4.7 g, 0.020 mol) was added. The reaction mixture was then refluxed for 48 h whereupon acetic acid was added to neutralize the remaining base. The ether solution was washed with water and evaporated to dryness, to leaving 7.3 g of a dark, semicrystalline mass. Flash chromatography of this on 300 g of silica with 3×250 ml + 10×100 ml of ethyl acetate-light petroleum (30:70) gave fractions (Nos. 5–13) containing a mixture of tetramethylsuccinimide, *N*-acetyl tetramethylsuccinimide and the desired product (as monitored by GLC). These fractions were combined and evaporated to dryness. Final purification was effected by sublimation at 120–130°C/0.1 mmHg which left behind pure $\text{T}_2\text{CHCOCH}_3$ (GLC); after recrystallization from hexane its m.p. was 162–166°C. ^1H NMR: δ 1.16 (s, ring CH_3), 2.16 (s, CH_3), 6.00 (CH). ^{13}C NMR: δ 20.8 (ring CH_3), 25.8 (CH_3), 61.7 (CH), 47.2 (C), 180.8 (CO in ring), 193.8 (CO). MS [CI-NH_3 , m/z (%)]: 382 ($M+15$, 60), 365 ($M+1$, 100); EI: 321 (15), 209 (19), 183 (19). Anal. $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_5$: C, H, N.

Preparation of N-(4-nitrobenzyl)tetramethylsuccinimide. Sodium (0.9 g, 0.039 mol) was dissolved in 200 ml of methanol and TH (6.07 g, 0.039 mol) was added. When all of the TH had dissolved, 4-nitrobenzyl bromide (8.45 g, 0.039 mol) was added and the mixture refluxed for 6 h. The mixture was poured into ice-water and the resulting solid was filtered, yield 10.5 g (93%), m.p. 75–80°C. After recrystallization of this from ethanol, 8.9 g (78% yield) of the pure compound were obtained, m.p. 85–87°C. Anal. $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4$: C, H, N.

Preparation of 2-(tetramethylsuccinimido)cyclohexanone. This compound was prepared as for the cyanomethyl derivative from TNa and 2-chlorocyclohexanone, yield 72%, m.p. 89–92°C, after recrystallization from diisopropyl ether. ^1H NMR: δ 1.19 and 1.20 ($2 \times$ s of 6 H each, $2 \times$ imide ring CH_3), 1.75 (m, 2 H, CH_2), 2.03 (m, 3 H, CH_2), 2.31 (m, 1 H, $J_{2,6}$ 0.93 Hz, 6- CH_{eq}), 2.56 (m, 2 H, J 13.1 Hz, 3- CH_2), 4.54 (ddd, 1 H, $J_{2,3,6}$ 13.1 Hz, $J_{2,3,ax}$ 6.3 Hz, $J_{2,6}$ = 0.95 Hz, 2-CH). ^{13}C NMR: δ 21.2 and 21.7 (imide ring CH_3), 24.5 (4- CH_2), 25.6 (5- CH_2), 29.4 (3- CH_2), 40.8 (6- CH_2), 46.9 (C in imide ring), 57.3 (2-CH), 182.5 (imide CO), 202.4 (ketone CO). MS [16 eV, m/z (%)]: 251 (M^+ , 100). Anal. $\text{C}_{14}\text{H}_{21}\text{NO}_3$: C, H, N.

Reaction between the T complex and cyclohexanone. T complex (63 mg) was dissolved in 1.0 ml of cyclohexanone and the solution was left at room temperature for 1 h. After the addition of bimesitylene as a GLC standard, the solution was analysed by GLC and found to contain TH (160% yield), 2-T-cyclohexanone (14%) and a large number of secondary products, the structures of which (GLC-MS) corresponded to products of elimination, oxidation and dimerization. These products were not further analysed or more thoroughly characterized, since the complexity of the secondary reactions did not in itself further the understanding of the substitution process.

Reaction between the T complex and phenylacetylene. Phenylacetylene (0.94 ml) was added at $t = 0$ to a solution of the T complex (1.26 g, 2.0 mmol) in 5.3 ml of acetonitrile, kept at 20°C. Samples (0.300 ml) were withdrawn at intervals and quenched by adding acetic acid (0.050 ml). After the addition of the internal standard (bimesitylene), the samples were analysed by GLC. 2-Bromo-1-phenylacetylene was formed in a maximum yield of 78% after ca. 5 min and was then gradually consumed in reactions with T^- (see below) over the following 16 h. After this period, the concentration of the bromo compound was approximately half of the maximum concentration.

Reaction of 2-bromo-1-phenylacetylene with Bu_4NT . Freshly distilled 2-bromo-1-phenylacetylene (294 mg, 1.62 mmol) was added to Bu_4NT

(182 mg, 0.46 mmol) in 0.80 ml of acetonitrile and the solution was left at room temperature for 70 h. After the reaction mixture had been quenched with acetic acid, and the internal standard (bimesitylene) had been added, analysis by GLC-MS showed the presence of the following components [yield (%): phenylacetylene (70) 1-phenyl-2-(tetramethylsuccinimido)acetylene (5), 2-(tetramethylsuccinimido)styrene (7), and α,β -dibromo- β -(tetramethylsuccinimido)styrene (74).

Preparation of α,β -dibromo- β -(tetramethylsuccinimido)styrene. Freshly distilled bromophenylacetylene (2.94 g, 16.2 mol) was added to a solution of Bu_4NT (1.8 g, 4.5 mmol) in 5 ml of acetonitrile and the solution left overnight at room temperature. After the volatile components had been evaporated, the residue was dissolved in 20 ml of diethyl ether and the solution washed with 2 M aqueous NaOH. Evaporation of the solution left a residue which was subjected to flash chromatography on silica. Elution with heptane (240 ml) and heptane-ether (400 ml; 9:1) produced eight 80 ml fractions, of which fractions 3-5 were pooled and evaporated to dryness. Recrystallization of the residual material from pentane gave 0.63 g (34% yield) of the title compound, m.p. 96-98°C. ^1H NMR: δ 1.10 and 1.25 (2 s, imide CH_3), 7.33-7.44 (m, C_6H_5). ^{13}C NMR: δ 21.0 and 21.3 (imide ring CH_3), 46.9 (imide ring C), 97.6 (C-2), 128.2, 128.6, 129.5, 134.1, 134.6 (aromatic C/C-1), 179.3 (CO). MS [Cl-NH_3 , m/z (%): 435 ($M+19$, 38), 434 ($M+18$, 20), 433 ($M+17$, 100), 431 ($M+15$, 63), 418 ($M+2$, 28), 417 ($M+1$, 17), 416 (M , 76), 414 ($M-2$, 43), 336 (11), 256 (52). Anal. $\text{C}_{16}\text{H}_{17}\text{Br}_2\text{NO}_2$: C: Found 47.3. Calc. 46.3, H, Br, N.

Preparation of methylenebis-N,N-tetramethylsuccinimide. Sodium (1.3 g, 0.057 mol) was dissolved in methanol (100 ml). TH (8.8 g, 0.057 mol) was then added and the resulting solution was evaporated to dryness. Diiodomethane (7.6 g, 0.028 mmol), acetonitrile (100 ml) and DMF (50 ml) were added and the mixture was refluxed overnight. The mixture was evaporated to dryness and water (250 ml) and diethyl ether-dichloromethane (350:50 ml) added. The organic layer was dried over magnesium sulfate and evaporated to dryness. The solid was recrystallized from toluene-hexane, to afford pure T_2CH_2 ,

7.4 g (81% yield), m.p. 156-159°C. ^1H NMR: δ 1.14 (s), 5.20 (s). ^{13}C NMR: δ 21.3 (CH_3), 41.9 (CH_2), 47.0 (C), 181.4 (CO). MS [m/z (%): 322 (M , 5), 266 (2), 183 (20), 168 (3). Anal. $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_4$: C, H, N.

Reaction between the T complex and tributylamine in benzene. T complex (6.31 g, 0.01 mol) and tributylamine (1.85 g, 0.01 mol) was refluxed for 24 h in 20 ml of benzene. The solution was then diluted with 75 ml of benzene and treated with 200 ml of diethyl ether. Crystals of tetrabutylammonium bromide (2.85 g, 89% yield) were filtered off. The filtrate was extracted with 3 \times 50 ml of 10% aqueous NaOH, washed with water and dried with magnesium sulfate. Evaporation then yielded 3.0 g of a thick oil which, upon being distilled in a short-path still, gave a major fraction (1.55 g, 63% yield) boiling at 210-220°C/0.5-0.8 mmHg. This consisted of the diastereomers of *N,N*-dibutyl-1,2-bis(tetramethylsuccinimido)butylamine according to its ^1H NMR spectrum: δ 0.85 (t), 1.2 (m), 1.34 (m), 2.50 (m) (for the signals of the *N,N*-dibutyl groups), 0.95 (2 \times t), 1.78 (m), and 1.50 (m), 4.55 (td, $J_{1,2}$ = 11.1 Hz), 5.64 (d, $J_{1,2}$ 11.1 Hz) (in order from the methyl group of the 1,2-bis-T-substituted butyl group), 1.06 and 1.08 (2 \times s) (ring methyl groups). MS [Cl-NH_3 (m/z): 506 ($M+15$), 492 ($M+1$).

Reaction between the T complex and acetonitrile. T complex (7.6 g, 0.0121 mol) was refluxed in acetonitrile (45 ml) for 45 h. A small sample was withdrawn for analysis of bromide ion (100% yield) and TH (136%). The major portion was evaporated to dryness and the residue treated with diethyl ether (200 ml); dichloromethane was not suitable here, since treatment with base led to the ultimate formation of T_2CH_2 which complicated the work-up of T_3CCN . Extraction of the ether solution with 0.25 M aqueous NaOH and evaporation to dryness left behind crude T_3CCN (0.44 g, 22%), m.p. after recrystallization from hexane 318-319°C. ^1H NMR: δ 1.22 (s). ^{13}C NMR: δ 21.3 (CH_3), 47.1 (ring C), 107.2 (CN), 179.3 (CO), C-CN not seen. MS [m/z (%): 500 (M , 2), 348 (12), 347 (72), 346 (20), 234 (13), 208 (9), 178 (4), 163 (4). Anal. $\text{C}_{26}\text{H}_{36}\text{N}_4\text{O}_6$: C, H, N.

Repetition of the experiment with 0.01 mol of the T complex in 50 ml of acetonitrile, followed by GLC analysis gave TH (132%), TCH_2CN (2%) and T_3CCN (21%).

Reaction between the T complex and TCH₂CN. T complex (2.0 g, 3.2 mmol) and TCH₂CN (0.31 g, 1.6 mmol) were refluxed in benzene for 40 h. GLC analysis of the reaction mixture showed the following components: TH (118%), TCH₂CN (27% recovered) and T₃CCN (51%).

Reaction between the T complex and N-cyanomethylphthalimide. T complex (2.0 g, 3.2 mmol) and N-cyanomethylphthalimide²³ (0.31 g, 1.7 mmol) were refluxed in benzene (35 ml) for 40 h. After the reaction mixture had been evaporated, diethyl ether (100 ml) was added. Stirring for 30 min followed by filtration gave an ether solution which contained only one component (GLC) after having been extracted with 0.025 M aqueous NaOH. The solution was concentrated to ca. 25 ml and left overnight in a refrigerator. Filtration gave 0.18 g of pure T₂(phthalimido)CCN, m.p. 219–220°C; a second crop (0.15 g) of the same m.p. was obtained from the mother liquor, total yield 42%. ¹H NMR: δ 1.249, 1.246 (s, CH₃), 7.84 (m, arom. H). ¹³C NMR: δ 21.3, 21.6 (CH₃), 47.2 (C), 107.4 (CN), 130.8 (C–CO in arom. ring), 124.2 (*ortho*-C), 134.9 (*meta*-C), 179.5 (succinimide ring CO), 164.8 (phthalimide CO), C–CN not seen. MS [*m/z* (%): 492 (*M*, 1), 339 (10), 226 (20), 200 (5), 174 (5).

Reaction between the T complex and acetone. T complex (0.449 g, 0.71 mmol) was dissolved in 6.0 ml of acetone at ambient temperature. The solution was allowed to stand for 10 min, during which time it underwent the usual colour phenomenon. The acetone was removed by evaporation. After the addition of a carefully weighed amount of bimesitylene (as a GLC standard), dry ether (15 ml) was added and the mixture stirred vigorously for 20 min. This procedure precipitated tetrabutylammonium bromide which was filtered off. The filtrate was evaporated to a volume of ca. 5 ml and analysed by GLC (3 m 5% OV-101 column, 140–260°C at 10 K min⁻¹). The yields (%) were: TH (119), TCH₂COCH₃ (54) and T₂CHCOCH₃ (28).

Reaction between the T complex and [²H₆]acetone. The reaction was carried out as for acetone, except that the reaction period was 35 min. The product yields (%) were: TH (118), TCH₂COCH₃ (59) and T₂CHCOCH₃ (47).

Reaction between the T complex and TCH₂COCH₃ in acetonitrile. The reaction was run in acetonitrile with 0.442 g (0.70 mmol) of the T complex and 0.153 g (0.72 mmol) of TCH₂COCH₃ at room temperature. After ca. 1 min, the reaction mixture was black–purple and the colour faded to yellow within 15 min. Work-up and analysis as above gave: TH (110%), recovered TCH₂COCH₃ (47%) and T₂CHCOCH₃ (58%, based on unrecovered starting material).

Reaction between the T complex and TCH₂COCH₃ in benzene. T complex (4.05 g, 6.4 mmol) and TCH₂COCH₃ (1.29 g, 6.1 mmol) were stirred in benzene (25 ml) for 1.5 h at 50°C. Evaporation of the reaction mixture and treatment with diethyl ether gave tetrabutylammonium bromide (1.37 g, 43 mmol) and an ether solution, containing TH (109%), TCH₂COCH₃ (6%) and T₂CHCOCH₃ (28%). A fourth major component (ca. 20%) was assigned the structure T₂CHCOCH₂T on the basis of its chemical behaviour (it was easily extracted into 1 M aqueous NaOH but not recoverable upon acidification) and mass spectrum: CI(NH₃): *m/z* of *M*⁺ = 517.

Reaction between the T complex and toluene. T complex (1.1 g, 1.75 mmol) was refluxed in toluene (30 ml) for 15 h. The mixture turned black and some black material was deposited. After the mixture had been filtered and evaporated, the residue was extracted with 100 ml of diethyl ether and the insoluble material (mainly Bu₄NBr) was filtered off. The solution was evaporated to a volume of 20 ml and analysed by GLC–MS. The main product (ca. 20% yield) was *N,N*-dibutyl-1,2-bis(tetramethylsuccinimido)butylamine; *N*-benzylsuccinimide was present in <1% yield.

Reaction between the T complex and 4-nitrotoluene. T complex (0.95 g, 1.51 mmol) and 4-nitrotoluene (0.41 g, 3.0 mmol) were refluxed in benzene (5 ml) for 16 h. GLC analysis of the reaction mixture showed the following product composition: TH (146%), 4-nitrotoluene (73% recovered) and *N*-(4-nitrobenzyl)tetramethylsuccinimide (54%). Identical experiments in acetonitrile and carbon tetrachloride gave TH (146, 156%), 4-nitrotoluene (82, 87% recovered) and 4-O₂NC₆H₄CH₂T (49, 49%). In all of the three experiments the detection of significant amounts

of tributylamine (63, 54 and 83 %, respectively) showed that the reaction between the T complex and tetrabutylammonium ion also took place: this aspect, however, was not further explored.

Attempted polymerization of methyl methacrylate by the T complex. T complex (156 mg) and acetone (200 μ l) were added to methyl methacrylate (2.0 ml, freshly distilled) and the solution allowed to stand at room temperature for 100 h. No polymerization occurred.

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