The Origin of Colour and EPR Spectral Phenomena During the Reaction between Acetone and the Tetrabutylammonium Tetramethylsuccinimide/*N*-Bromotetramethylsuccinimide Complex

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The reaction between the tetrabutylammonium tetramethylsuccinimide/*N*-bromotetramethylsuccinimide complex (the T complex) and acetone produces a transient purple colour and an EPR signal (a quintet). These phenomena accompany the main reaction, which consists of successive brominations/tetramethylsuccinimido substitutions of acetone. With two of the consecutively formed products, tetramethylsuccinimidoacetone and 1,3-bis(tetramethylsuccinimido)acetone, the same phenomena appear with successively increasing intensity and also earlier during the reaction course. It is suggested that the purple colour originates in the monobromination of 1,3-bis(tetramethylsuccinimido)acetone, followed by proton abstraction and bromide loss to give the 1,3-bis(tetramethylsuccinimido)-2-oxidoallyl species. This oxyallyl derivative is a true zwitterionic chromogen, analogues of which are known to display similar colours.

The EPR signal was shown to originate from a related oxyallylic species, 1,3-dibromo-1,3-bis(tetramethylsuccinimido)-2-oxidoallyl radical cation, a representative of a novel class of intermediate, ylidions. The same signal could be produced by treating either 1,1,3,3-tetrabromoacetone or pentabromoacetone with the T complex. A related ylidion, the radical cation of 2,3-bis-(*N*,*N*-diethylamino)cyclopropenone, was generated as a model.

Suitable six-carbon 1,4-diketones, such as hexane-2,5-dione or cyclohexane-1,4-dione, upon treatment with the T complex gave solutions containing high concentrations of the radical anion of tetrakis(tetramethylsuccinimido)-1,4-benzoquinone.

In a previous paper,[1] the reaction between acetone and the tetrabutylammonium tetramethylsuccinimide/*N*-bromotetramethylsuccinimide complex (in the following to be abbreviated either as $Bu_4N^+ T_2Br^-$ or as the 'T complex') was shown to proceed via a polar mechanism along its major pathway, substitution of T into the C–H bonds of acetone – and indeed of other C–H acidic compounds. The postulated mechanistic scheme is shown in eqns. (1)–(6). It

$$T_2Br^- \rightleftharpoons T^- + TBr \quad (1)$$

$$T^- + RH_2 \rightleftharpoons TH + RH^- \quad (2)$$

$$RH^- + TBr \rightarrow RHBr + T^- \quad (3)$$

$$RHBr + T^- \rightarrow RHT + Br^- \quad (4)$$

$$RHT + T^- \rightleftharpoons RT^- + TH \quad (5)$$

$$RT^- + RH_2 \rightleftharpoons RTH + RH^-, \text{ etc.} \quad (6)$$

$RH_2 = CH_3COCH_3$

is assumed that the complex in itself is kinetically inert and that base attack by T^- upon a C–H bond of the substrate constitutes the rate-determining step. The enolate ion formed is brominated by TBr in an X-philic step,[2] and the first stable product, TCH_2COCH_3, is formed in an S_N2 step between bromoacetone and T^-. Being a stronger acid than acetone by a factor of approximately 10^3, TCH_2COCH_3 is converted into its conjugate base which (a) is brominated by TBr and ultimately is transformed into $T_2CHCOCH_3$ and TCH_2COCH_2T and (b) acts as a catalyst for the first substitution step [eqn. (6)]. The net result is a strongly autocatalytic reaction.

The reaction between acetone and the T complex is accompanied by a peculiar colour phenomenon, in that the originally colourless solution after a certain induction period assumes a purple colour, the intensity of which goes through a sharp maximum during a period of 2–15 min, depending upon reaction conditions. Fig. 1 shows the variation in absorbance at 557 nm with time in acetone-d_6, this particular solvent being chosen to make possible a comparison with the time variation of an EPR signal from the reacting solution (see below). The time taken to reach the colour maximum is reproducible to within ± 2 % and coin-

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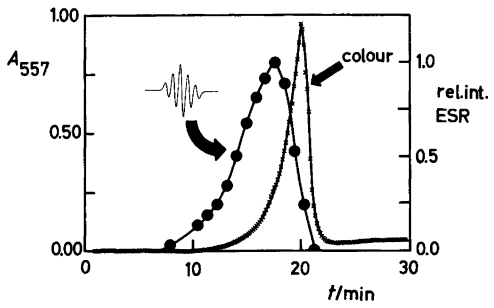


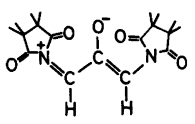
Fig. 1. Time dependence of the purple colour and EPR signal at 22 °C in acetone-d_6.

cides with the end-point of the reaction, defined as the formation of the first product, TCH_2COCH_3.[1]

The reaction was EPR active, in that a quintet developed after a certain time, went through a maximum and eventually disappeared rather abruptly. In neat solvent this signal was only seen in hexadeuterioacetone (Fig. 1), presumably due to more favourable kinetic conditions than in acetone. In acetonitrile or dichloromethane, the same signal was however clearly seen at acetone concentrations between 0.2 and 0.8 M (see below). The parameters of the signal (line intensities 1:2:3:2:1, $a = 0.201$ mT, $g = 2.00462$ in dichloromethane) indicated the presence of a radical species in which the odd electron is coupled to two chemically equivalent nitrogen atoms.

The conclusion of the previous paper was that the colour and EPR phenomena are due to side reactions and do not reflect molecular events along the major product-forming pathway. Nevertheless, the reproducibility and striking appearance of these phenomena enticed us to try to elucidate their mechanistic background, in spite of the sometimes rather fruitless experiences of chemists chasing transient colours. Also, the nature of a chromophore originating from such a fairly simple aliphatic system might be of some general interest. Finally, some electron transfer chemistry of possibly principal interest must be going on in the system, since radical species are formed from closed-shell species.

We now report the results of EPR spectral studies and other experiments designed to shed light on the nature of



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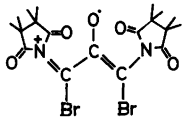

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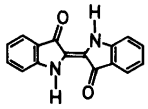
the coloured and EPR-active species. It would appear that the phenomena described above in all probability must be due to tetramethylsuccinimido-substituted oxyallylic species, in that the violet colour and EPR signal correspond to the 1,3-T_2-oxyallyl zwitterion **1** and the 1,3-dibromo-1,3-bis-T_2-oxyallyl radical cation **2**, respectively. The arguments for these assignments are presented below. In addition, the reaction between the T complex and several six-carbon atom 1,4-diketones were found to give strongly EPR-active solutions of the radical anion of tetrakis-(tetramethylsuccinimido)-1,4-benzoquinone.

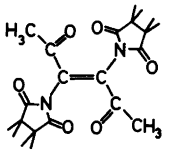
Results and discussion

From the outset, this study was pursued along several lines with different guiding hypotheses regarding the nature of the coloured and EPR-active species. One idea had already been eliminated in the previous study,[1] namely that the T substitution of acetone proceeds according to an $S_{RN}1$-like mechanism, with a radical or radical anion formed along the main reaction pathway being responsible for these phenomena. The reaction is not simply a radical chain reaction but a conventional polar process, although with some rather unexpected consequences with regard to products. Moreover, the electrochemical properties (reduction potentials at < -1.3 V) of two plausible radical anion precursors (T_2, $T_2CHCOCH_3$) were not compatible with the fairly high chemical stability of the unknown species in the presence of a moderately strong ET oxidant, *N*-bromotetramethylsuccinimide (TBr).[3]

A second idea is centred on the possibility that a dimer of the original three-carbon system might be the source of the unknown species. It is easy to recognize an indigo-like chromophore in, for example, the dehydro dimer of TCH_2COCH_3, $T(CH_3CO)C{=}C(COCH_3)T$, that might cor-



Indigo



respond to or be related to the purple species. Moreover, a six-carbon chain is, in principle, convertible into a six-ring system where species with the desired properties are easier to find, like, for example, suitably substituted quinones. A third line of hypothesis explores the possibility that oxyallyl zwitterion/cyclopropanone(enone) intermediates[4] play a critical role in colour/radical formation. The treatment presented below mainly follows the logic outlined above, although it cannot be avoided that the chronological development of events sometimes is reflected.

Structure of the purple species. We have already pointed out[1] that the use of the products of two consecutive tetramethylsuccinimido substitutions of acetone leads to a dramatic increase of the intensity of the purple colour and a substantial decrease in the time (τ) required to reach the maximum of the colour intensity. This is shown in Fig. 2, where A_{557} (absorbance at 557 nm) is plotted vs. time for reaction between the T complex and acetone, TCH_2COCH_3 and TCH_2COCH_2T, respectively, in acetonitrile. For a more precise measure of the amount of colour

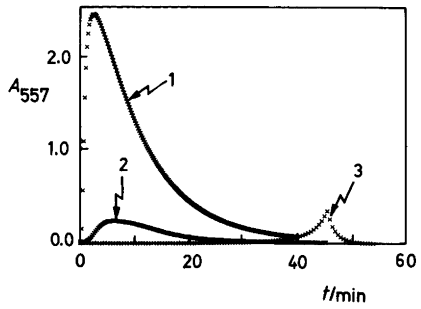


Fig. 2. Time dependence of the absorbance at 557 nm recorded from a solution of (1) 12 mM T complex and 1.0 mM TCH_2COCH_2T; (2) 108 mM T complex and 10.8 mM TCH_2COCH_3; and (3) 107 mM T complex and 440 mM acetone in acetonitrile at 20 °C.

produced, the area under these curves was integrated and denoted *Int.*[1] With corrections for differing initial substrate concentrations the *Int* values fall in the ratios 1:81:7340 for acetone, TCH_2COCH_3 and TCH_2COCH_2T, not far from the ratios expected for the reasonable assumption that the rate of the first substitution process is identical with that of the second, 1:81:6560.

In one experiment in acetone-d_6, the purple colour was frozen out at its maximum intensity by fast cooling of the reaction vessel to −80 °C. At this temperature, the colour was stable for many hours. The solution displayed no EPR signal at −80 °C, nor did any signals appear upon slow warming to room temperature. Thus we conclude that the purple species is not a radical.

The second isomer of T_2-acetone, $T_2CHCOCH_3$, after thorough purification showed no colour whatsoever upon treatment with the T complex.

The A_{557}/time curve for TCH_2COCH_2T showed no sign of an induction period (Fig. 2), showing that the colour-forming reaction cannot be many steps away from TCH_2COCH_2T. This is seen in Fig. 3, where *Int* is plotted vs. $[\text{T complex}]_0$; for full colour development only 2.3 mol of the T complex are required per mol of TCH_2COCH_2T. It appears reasonable to assume that the actual ratio is 2:1, given the experimental imperfections of the system.

An NMR experiment was performed to see if any time-dependent signals could be observed during the course of

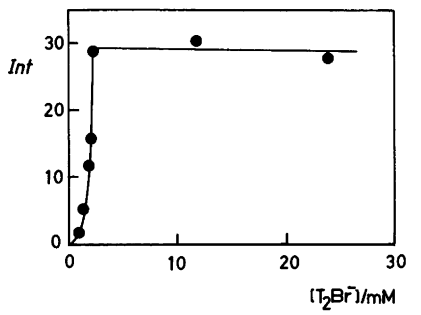


Fig. 3. Variation of *Int* with $[T_2Br^-]$ from the reaction between the T complex and TCH_2COCH_2T (1.01 mM) in acetonitrile at 20 °C.

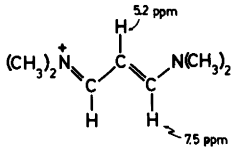
the T complex/TCH_2COCH_2T reaction (initial concentrations in CD_3CN, 30 and 16 mM, respectively; probe temperature ca. 24 °C). The solution turned dark purple after a few seconds and the colour disappeared after 25 min. The first spectrum, taken after 2 min, showed that all of the TCH_2COCH_2T had disappeared. Several new signals had grown up but only one, a singlet at 5.46 ppm, subsequently diminished in intensity (12 min) and eventually disappeared completely (25 min). This concentration/time behaviour is approximately the same as that exhibited by the purple colour, given the difference in temperature between the experiments.

Putting these pieces of evidence together, we postulate that the coloured species is an oxyallyl zwitterion, formed by bromination of TCH_2COCH_2T and subsequent deprotonation/bromide ion loss [eqns. (7)–(8)]. The oxyallyl

$$TCH_2COCH_2T \xrightarrow{T_2Br^-} TCH(Br)COCH_2T \quad (7)$$

$$TCH(Br)COCH_2T + T^- \rightarrow \underset{\mathbf{1}}{T\overset{+}{C}HCO\overset{-}{C}HT} + Br^- + TH \quad (8)$$

zwitterion of eqn. (8) is identical with species **1** above. The mechanism has the right characteristics for fitting with experimental data: two moles of the T complex per mole of TCH_2COCH_2T are required to form **1**, and only one NMR singlet is seen to change in the required way during the reaction. Species **1** is a derivative of a cyanine dye system (**3**), for which the NMR shifts are known.[5] It is entirely



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reasonable that the signal of the α-hydrogen might experience an upfield shift of ca. 1.7 ppm upon substitution of the β hydrogen by a negatively charged oxygen. Unfortunately, to our knowledge, no NMR data are available for oxyallylic cations, so that this conclusion must still rest upon conjecture.

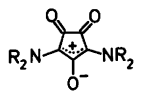
At first sight, the oxyallyl cation **1** does not seem to fit the requirements for possessing an absorption maximum around 557 nm. The λ_{max} value of **3** is 313 nm,[6] and it is not immediately obvious how substitution at the middle carbon by $-O^-$ can cause a bathochromic shift of ca. 240 nm, especially since the nitrogens are formally involved in cross-conjugation with the imide oxygens. However, precedent for the large shift is known. Species **1** is a true zwitterionic chromogen[7] for which no neutral resonance form can be written, and for such a case bathochromic shifts of the type mentioned above are feasible. A known, simple example is derived from the *N*-methylquinolinium ion which experiences a bathochromic shift of ca. 170 nm upon sub-

Table 1. Absorbance maximum of colour produced during the reaction of the T complex with acetone in different media.

Medium	[Acetone]/mM	λ_{max}/nm
Benzene	4600	560
Acetonitrile	440	554
Acetonitrile/18.5 mM water	440	550
Acetonitrile/480 mM water	440	538
Acetonitrile/390 mM methanol	440	552
Acetonitrile/1500 mM methanol	440	550

stitution by $-O^-$ in the 8-position (λ_{max} moves from 315 to 484 nm in ethanol[8]). It is also known (and in fact often utilized in the form of the Dimroth–Reichardt E_T scale for solvent polarity[9]) that this type of absorption maximum is very sensitive towards solvent polarity, making possible a test of the nature of the purple species. Table 1 shows the variation of λ_{max} with change in solvent composition, bearing in mind that the solubility of the T complex severely limited the range and composition of solvents that could be used and that the extinction coefficient of the band was strongly lowered by the addition of polar solvents. One can still see that the influence of a polar additive such as water is strong, which supports the zwitterionic nature of the purple species. A separate experiment established that the purple species was not extractable into pentane from acetonitrile to any extent.

Finally, the cross-conjugation problem is alleviated by the fact that **1** actually possesses a backbone of eight sp^2 hybridized atoms, proceeding from an imide carbonyl in one ring to the imide carbonyl in the second ring. In combination with the arguments presented above, the formulation of the purple species as **1** agrees with known facts and accepted ideas. Stable, coloured molecules with bis-amino substituted oxyallyl structures are known[10] and some examples are shown below (**4** and **5**). It is to be expected that a bis-imido species should be less stable.



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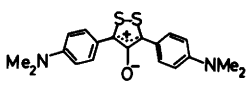
λ_{max} = 440–450 nm



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λ_{max} = 606 nm

A known reactivity mode of oxyallyl is [4+3]-cycloaddition with a diene, such as furan. However, furan concentrations of up to ca. 1.5 M did not affect the intensity or time development of the purple signal. We plan to extend this reaction type to more reactive dienes and content ourselves by noting that oxyallyls substituted by a donor group (alkoxy, arylthio) either do not react with furan or undergo the reaction only reluctantly.[11]

We have also explored the dimer hypothesis in order to explain the formation of the purple-coloured species. As

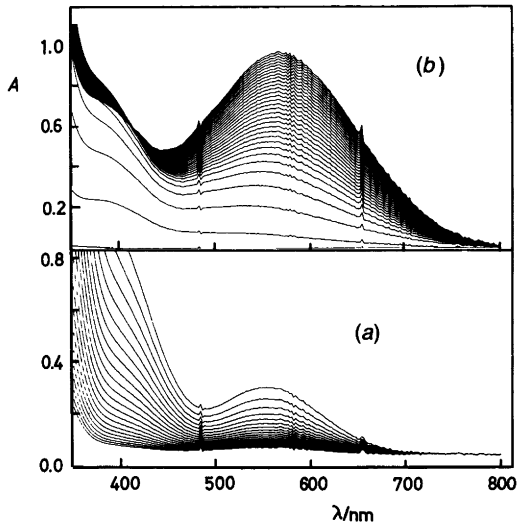


Fig. 4. Repetitive scans of solutions of (*a*) 107 mM T complex and 440 mM acetone (40 s between spectra, only spectra from rising part included) and (*b*) 107 mM T complex and 1.1 mM cyclohexane-1,4-dione (300 s between spectra) in acetonitrile at 20 °C.

outlined in more detail below, this assumes that two acetone fragments somehow dimerize to a linear six-carbon compound from which one is able to gain access to six-ring systems. As a consequence, the cyclohexane-1,4-dione and ultimately the tetrakis(tetramethylsuccinimido)benzoquinone (**6**) system should be within reach. Indeed, treatment of cyclohexane-1,4-dione at the 1 mM level with the T complex (100 mM) in acetonitrile gave a beautifully purple-coloured solution [λ_{max} = 568 nm; Fig. 4(*b*)]. This was, however, for all practical purposes indefinitely stable (days/weeks vs. min) compared with the unknown purple colour from the acetone reaction [Fig. 4(*a*)], and we therefore exclude this alternative. When **6** was subjected to the same reaction, a pink, stable solution was formed after 3–4 h (λ_{max} = 498 nm), again with no obvious relationship to the unknown purple colour.

Structure of the EPR-active species. As mentioned in the introduction, the treatment of acetone with the T complex in that solvent (Fig. 1) or acetonitrile produced an EPR signal (a 1:2:3:2:1 quintet, Fig. 5) at, maximally, the 10^{-6} M concentration level with a concentration/time beha-

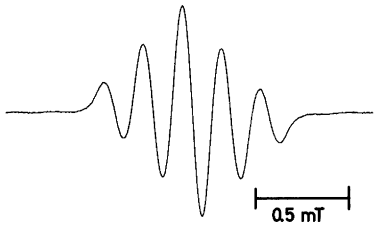


Fig. 5. Quintet from a solution containing T complex (0.37 mM) and 1,1,3,3-tetrabromoacetone (0.11 M) in acetonitrile at 20 °C. See Table 2.

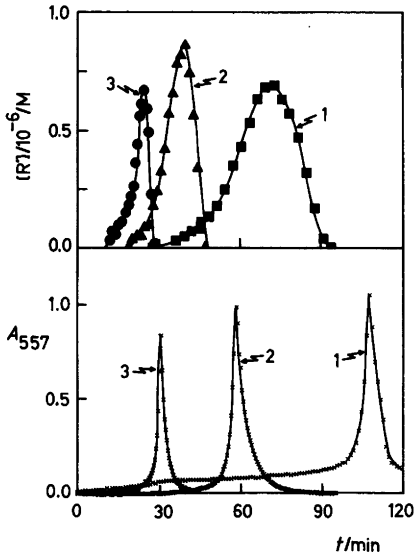


Fig. 6. Time behaviour of absorbance at 557 nm (lower curves) and radical concentration (upper curves) from solutions of 340 mM T complex and (1) 170 mM; (2) 340 mM; and (3) 680 mM acetone in acetonitrile at 20 °C.

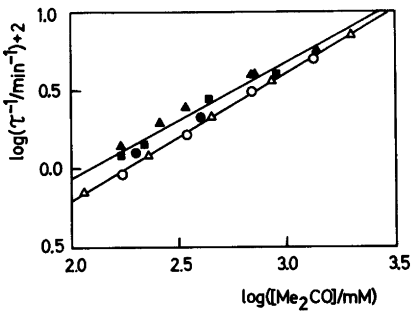


Fig. 7. Dependence of $\log(\tau^{-1}/10^{-2}\ \text{min}^{-1})$ with $\log([\text{acetone}]_0/\text{mM})$ for the purple colour (lower line, open symbols: and EPR signal (upper line, filled symbols) in acetonitrile at 20 °C. △, 100 mM; ○, 340 mM T complex; ●, 100 mM; ■, 220 mM; ▲, 340 mM T complex.

viour analogous, but not identical with that of the purple colour. The same behaviour was found when the reaction was run in acetonitrile, as is evident from Fig. 6, where the colour is seen to trail the EPR signal. The time difference between the two phenomena is also illustrated in Fig. 7,

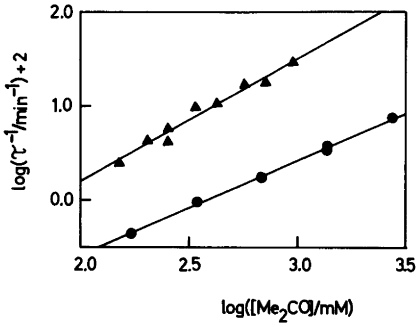


Fig. 8. Dependence of $\log(\tau^{-1}/10^{-2}\ \text{min}^{-1})$ with $\log([\text{acetone}]_0/\text{mM})$ for the EPR signal in dichloromethane at 20.0 °C (●) and 40.0 °C (▲). [T complex] 340 mM.

where $1/\tau$ (τ = the time taken to reach the maximum colour or radical concentration) is used as a kinetic parameter of unit 1/time in the same way as in our previous paper.[1] In both cases τ is of order 0.8 in $[\text{acetone}]_0$. The signal could equally well be seen in dichloromethane, although we are less sure about the quantitative aspects due to the competing reaction[1] between dichloromethane and T^-. Fig. 8 shows plots of $\log(1/\tau)$ vs. $[\text{acetone}]_0$ at two temperatures, both with slopes around 1.

The course of the reaction could also be monitored in yet another way, which confirmed its autocatalytic nature. Owing to the change in the dielectric properties of the reacting solution, the bias current of the EPR spectrometer increased strongly during the run. Plots of bias current vs. time are shown in Fig. 9 for the three runs already highlighted in Fig. 6. As shown before,[1] the break in the curve coincides with the maximum intensity of the purple colour, whereas the maximum radical concentration is reached already in the first portion of the ascending part.

As in the case of the colour, the use of TCH_2COCH_3 or especially TCH_2COCH_2T as the substrate gave much higher radical concentrations, maximally ca. 0.1 mM in the latter case. The stability of the radical also was much higher, of the order of days or even weeks under suitable conditions (Table 2). The maximum radical concentration attainable from TCH_2COCH_2T was strongly dependent upon $[\text{T complex}]_0$, the reaction being approximately third order, but showed essentially no dependence upon $[TCH_2COCH_2T]_0$ at constant $[\text{T complex}]_0$.

Table 2. EPR parameters for the quintet obtained in different systems.

Method of preparation	g	a_N/mT	k_{decay}/min^{-1}
Acetone + T complex in dichloromethane	2.00462	0.201	
Hexadeuterioacetone, neat + T complex	–	0.206	
TCH_2COCH_2T + T complex in acetonitrile	2.00459	0.213	7×10^{-3}
			1.2×10^{-3}
TCH_2COCH_2T + T complex in acetonitrile/ 0.1 M $NaClO_4$	–	0.213	1.1×10^{-4}
TCH_2COCH_2T + T complex in acetonitrile/ 0.4 M Bu_4NBr	–	0.216	7×10^{-2}
1,1,3,3-Tetrabromoacetone + T complex in acetonitrile	2.00462	0.215	1.2×10^{-3}
			3.9×10^{-3}
Pentabromoacetone + T complex in acetonitrile	2.00454	0.215	

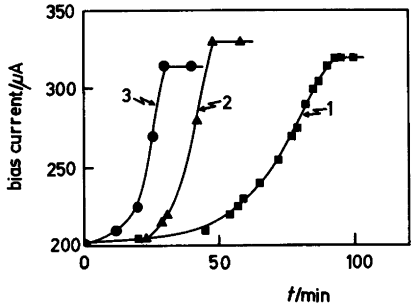


Fig. 9. Bias current vs. time for solutions of 340 mM T complex and (1) 170 mM; (2) 340 mM; and (3) 680 mM acetone in acetonitrile at 20 °C.

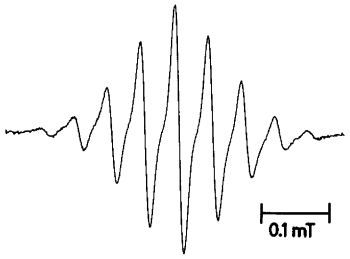


Fig. 10. Nonet from a solution of tetrakis-(tetramethylsuccinimido)-1,4-benzoquinone radical anion (prepared by Na reduction of **6**) in acetonitrile at 20 °C. See Table 3.

The dimer hypothesis assumes that some mechanism gives rise to a six-carbon compound from a suitably substituted acetone. As an example, TCH_2COCH_3 might undergo bromination to give $TCH(Br)COCH_3$ which in turn could react with the enolate ion of TCH_2COCH_3 [eqn. (9)]

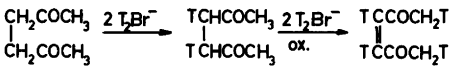
$$TCH(Br)COCH_3 + (TCHCOCH_3)^- \rightarrow \underset{\underset{\mathbf{7}}{TCHCOCH_3}}{\overset{TCHCOCH_3}{|}} + Br^- \quad (9)$$

to give **7**. Even if this reaction occurs as a second-order reaction between components of low concentration, it might still take place with an efficiency high enough to produce radicals at the 10^{-6} M concentration level also when acetone is the starting material. Once the six-carbon fragment is formed, feasible mechanisms for cyclization are available, as shown below.

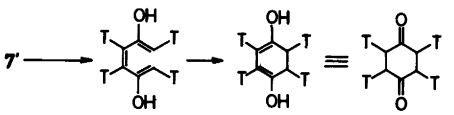
Model six-carbon compounds were found in hexane-2,5-dione, cyclohexane-1,4-dione and **7**, prepared by reaction between Bu_4NT and 3,4-dibromohexane-2,5-dione. On treatment with the T complex in acetonitrile, 5–10 mM solutions of either of these compounds produced an identical, very strong EPR signal, a 1:4:10:16:19:16:10:4:1 nonet (Fig. 10) indicating coupling of the unpaired electron to four equivalent nitrogens with EPR parameters as listed in Table 3. When prepared from the T complex, the nonet was stable for hours, sometimes also over periods of several days. The same signal was obtained upon sodium reduction of tetrakis(tetramethylsuccinimido)-1,4-benzoquinone (**6**) in acetonitrile. The latter sample was stable indefinitely, showing practically no decrease in radical concentration after 6 months.

In view of the relatively high stability of the nonet in the presence of TBr, an ET oxidant of medium strength[3] (it oxidized ferrocene to ferricinium ion with rate constants of the order of 1 $M^{-1}\,s^{-1}$), the electrochemical properties of **6** were studied using cyclic voltammetry (CV). It gave an almost reversible cathodic one-electron couple with $E^{\circ\prime}$ = 0.29 V vs. NHE and a second irreversible one-electron couple of $E^{\circ\prime} \approx -0.79$ V vs. NHE (peak separation ca. 800 mV at a sweep rate of 100 mV s^{-1}). This should be compared with the successive $E^{\circ\prime}$ values of tetrabromo-1,4-benzoquinone which were found to be 0.18 and −0.62 V (peak separations 80 and 175 mV, respectively, at a sweep rate of 100 mV s^{-1}). The electrochemical properties of **6** are compatible with the stability of its radical anion in the EPR experiments vs. oxidation by TBr.

Thus, suitable six-carbon compounds do give high concentrations of $\mathbf{6}^{-\cdot}$ upon treatment with the T complex in acetonitrile. The mechanism of this transformation can presently only be subject to speculation, but a facile mechanism could take the form of reactions of eqns. (10)–(12),



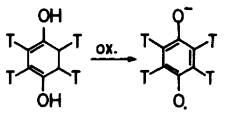
(10)



(11)

Table 3. EPR parameters for the nonet obtained in different systems.

Method of preparation	*g*	a_N/mT
Hexane-2,5-dione + T complex in acetonitrile	2.00527	0.0491
Hexane-2,5-dione + T complex in dichloromethane	2.00535	0.0488
3,4-Bis(tetramethylsuccinimido)hexane-2,5-dione (**7**) + T complex in acetonitrile	2.00528	0.0491
Cyclohexane-1,4-dione + T complex in acetonitrile	2.00527	0.0493
Tetrakis(tetramethylsuccinimido)-1,4-benzoquinone (**6**) + Na in acetonitrile	2.00526	0.0495

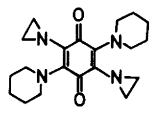


(12)

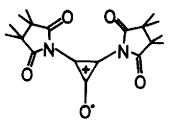
$6^{-\cdot}$

starting from hexane-2,5-dione and incorporating **7** as well. The behaviour of cyclohexane-1,4-dione can be simply accommodated by assuming quadruple T substitution at the four carbons, followed by oxidation to $6^{-\cdot}$.

What bearing does this reaction have on the nature of the species giving rise to the quintet? In fact, the nonet has never been detected from any reaction involving a three-carbon precursor (from literally hundreds of attempts) and thus it would seem to excluded it from consideration. However, in view of the fact that radical anions of closely related tetraamino derivatives of benzoquinone (for example **8**) are known to give quintets of similar appearance,[12] it is important to know that $6^{-\cdot}$ does give a nonet.



8



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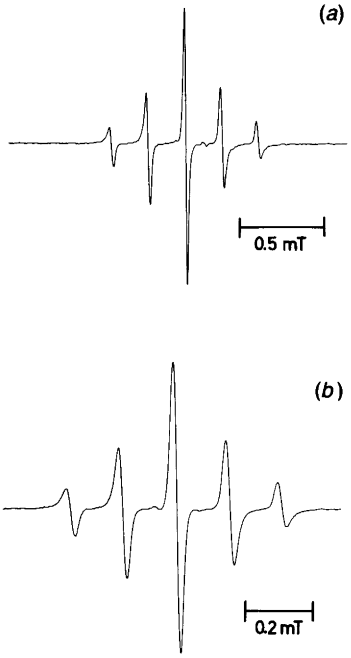


Fig. 11. Quintets from (*a*) $T_2CO^{-\cdot}$ and (*b*) $TCOCOT^{-\cdot}$ (prepared by sodium reduction of the parent compounds) in the presence of Bu_4NT (0.2 M) in acetonitrile at 20 °C.

Secondly, other 1,4-benzoquinone species might give the quintet, for example, the radical anion of the 2,3-dibromo-4,5-(T_2)-substituted derivative. It was therefore of interest to find out the approximate relationship between the stabilities of the two radicals when generated simultaneously. A series of EPR experiments established that equal intensities of the quintet and nonet are present after 5 min in a solution initially 27 mM in TCH_2COCH_2T, 0.077 mM in **6**-H_2 (ratio between substrates ca. 350) and 0.3 M in the T complex. The nonet however disappeared much faster than the quintet, being essentially consumed after 1 h (half-life ca. 10 min). The intensity of the quintet did not change at all over this period. This shows that the nonet might, in principle, be formed from the quintet but remain undetected owing to its much lower stability, provided the conditions are correct with respect to concentrations. Thus the above experiments excluded that the quintet is due to $6^{-\cdot}$ but not that the dimer pathway actually takes place to some extent.

The second hypothesis, involving oxyallylic/cyclopropanone species as intermediates, likewise had several branches that had to be pursued. A likely pathway from $TCH(Br)COCH_2T$ would be cyclization to give 2,3-(T_2)-cyclopropanone which, by further oxidation, might end up in a radical ion of 2,3-(T_2)-cyclopropenone (**9**), a reasonable candidate for a 1:2:3:2:1 quintet. By analogy to the known behaviour[4,13] of the corresponding diphenyl species, traces of oxygen and/or water might convert the radical anion into other possible quintet-generating species, like $T_2CO^{-\cdot}$ ot $TCOCOT^{-\cdot}$, both expected to be fairly stable.

The two latter radical ions can be summarily excluded from further consideration, since the parent compounds could easily be prepared and converted into radical anions by sodium reduction under basic conditions (in acetonitrile with Bu_4NT present) with EPR characteristics different from those of the unknown quintet (Fig. 11; cf. Table 2).

The radical anion of 2,3-(T_2)-cyclopropenone can most likely be excluded from consideration by its expected ease of oxidation. Attempts to synthesize this compound so far have failed, but the model compound, 2,3-bis(*N,N*-diethylamino)cyclopropenone,[14] was not reduced cathodically above −2.0 V vs. NHE, and although the presence of tetramethylsuccinimido groups instead of Et_2N groups is likely to increase the redox potential, it would presumably

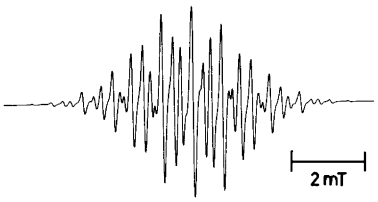


Fig. 12. EPR spectrum of the radical cation of 2,3-bis(*N,N*-diethylamino)cyclopropenone ($9^{+\cdot}$), prepared by oxidation of **9** by tris(4-bromophenyl)aminium hexachloroantimonate in acetone.

not move into the region 0.2–0.3 V vs. NHE, known from the case of **6**/**6**$^{-\cdot}$ to be required for adequate stability of a radical anion in the presence of an excess of T_2Br^-. Another possible species is the radical cation of 2,3-(T_2)-cyclopropenone (**9**$^{+\cdot}$); this was again excluded on the basis of a comparison with 2,3-bis(*N,N*-diethylamino)cyclopropenone which showed a quasireversible couple with $E^{o\prime}$ at 0.92 V vs. NHE (Pt anode, 100 mV s^{-1} sweep rate, peak separation 95 mV) in acetonitrile. The radical cation could not be generated for EPR observation by treatment of the parent compound with the T complex. Treatment with tris-(4-bromophenyl)aminium hexachloroantimonate in acetone or dichloromethane however gave a yellow–brown solution of the radical cation (Fig. 12) which survived for a short period only, ca. 20 min. The radical cation of 2,3-(T_2)-cyclopropenone is expected to be much less stable and therefore it is unlikely that it corresponds to the quintet.

Radical cations of the above type (**2** and **9**) are relatively stable members of a new class of reactive intermediate, ylidions or radical cations formed via one-electron oxidation of ylides,[15] as for example phenacyl sulfonium ylides [eqn. (13)].

$$PhCO-\overset{-}{C}H-\overset{+}{S}R_2 \xrightarrow{-e^-} PhCO-\overset{\cdot}{C}H-\overset{+}{S}R_2 \qquad (13)$$

The hypothesis that an oxyallylic species might be the origin of the quintet eventually led us to consider the dibromo-bis-(T_2)-substituted radical cation **2**. Such a species might be formed via a triple bromination of TCH_2COCH_2T by T_2Br^-, followed by proton/bromide ion loss from $TC(Br)_2COCH(Br)T$ and one-electron oxidation ultimately to give **2**. Alternatively, a double bromination might suffice, but then a hydrogen must be oxidized off before the final one-electron oxidation step. Although these schemes seem to require a rather intricate interplay of kinetic factors, they have the advantage of being easily testable from quite a different starting point, namely to let the T complex react with either pentabromoacetone or 1,1,3,3-tetrabromoacetone, corresponding to the two possibilities outlined above. Gratifyingly, on treatment of either of these bromoacetones with the T complex, high concentrations of a radical identical with the unknown quintet from TCH_2COCH_2T were detectable (Table 2).

The formulation of the radicaloid species **2** as a radical *cation* and not the anion rests on several pieces of evidence. Firstly, halogen-substituted radical anions are normally very unstable with respect to loss of halide ion, as known from a large number of cases.[16] Secondly, the stability of the quintet was strongly influenced by the nature of the anion present. The addition of perchlorate ion increased its stability by more than a factor of ten, whereas an excess of bromide ion decreased it equally as much (Table 2). This behaviour is expected for a cationic species engaged in ion pairing with the various counter-ions present in the solution, but not for an anionic one.

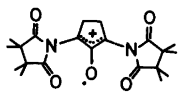
A number of other ketones were tested for possible EPR signals appearing upon treatment with the T complex.

Table 4. EPR signals from the reaction between different ketones and the T complex.

Compound	Solvent[a]	EPR signal
Methyl ethyl ketone	Neat	Broad, not resolved
Methyl ethyl ketone	DCM	Asymmetric, resolved
Diethyl ketone	Neat	Broad, very weak
Diethyl ketone	DCM	No signal
Methyl isopropyl ketone	Neat or DCM	No signal
Methyl t-butyl ketone	Neat or DCM	No signal
Diisopropyl ketone	DCM	No signal
$T_2CHCOCH_3$	DCM	No signal
Acetophenone	Neat	Broad, deformed
Benzyl methyl ketone	DCM	Broad, unresolved weak
Cyclopentanone	AN	Quintet of quintets[b]
Cyclohexanone	DCM	9-lines, not fully symmetrical
Cycloheptanone	AN	Broad, unresolved, weak
Indan-2-one	AN	Broad, unresolved
Butane-2,3-dione	DCM	Septet of quintets
Pentane-2,4-dione	DCM	Broad, distorted
Indan-1,3-dione	DCM	No signal

[a]DCM = dichloromethane, AN = acetonitrile. [b]Right wing only partially resolved.

Since the formation of **2** uses all available hydrogens in acetone, it is not possible to formulate analogous species from any type of substituted acetone. In keeping with this, most ketones employed gave no or weak EPR signals, mostly rather undefined and/or unsymmetrical (Table 4). Notable exceptions were the cyclopentanone and biacetyl reactions, the EPR spectral behaviour of which will be dealt with in a later publication. In particular, the radical species from cyclopentanone warrants interest, since the hyperfine splitting pattern (quintet of quintets with hfs values of ca. 0.058 and 0.32 mT, respectively) might well correspond to the ylidion **10**.



10

Experimental

Materials. Acetone (analytical grade), acetonitrile (UVASOL^R from Merck Co.) and dichloromethane (Pestanal^R from Merck Co.) were stored over molecular sieves (3 Å). Tetramethylsuccinimidoacetone,[1] 1,1,3,3-tetrabromoacetone,[17] pentabromoacetone[17] and 2,3-bis(*N,N*-diethylamino)cyclopropenone[14] were prepared according to known methods.

Spectra. ^1H and ^{13}C NMR spectra (in $CDCl_3$) were recorded on a Nicolet 300 MHz instrument, chemical shifts being

given downfield with respect to $SiMe_4$. GLC/MS spectra were recorded on a Finnigan 4021 instrument of 70 eV. UV/VIS spectra were recorded on an HP-8452 diode-array spectrophotometer equipped with a Chem Station. Samples for EPR measurements were prepared under argon in quartz tubes of ca. 1 or 3 mm i.d. and spectra were recorded on a Bruker ER 200D-SRC spectrometer, equipped with 100 kHz modulation and controlled by an Aspect 3000 computer. Concentrations were measured relative to samples of known spin content (solid DPPH) contained in capillary tubes.

Tetrakis(tetramethylsuccinimido)-1,4-benzoquinone (**6**).[18] Sodium (0.30 g, 13 mmol) was dissolved in methanol (50 ml) and tetramethylsuccinimide (2.15 g, 14 mmol) was added to the solution. The solution was evaporated to dryness, whereafter a solution of 0.80 g (3.3 mmol) of chloranil in acetonitrile (35 ml) was added and the deep purple mixture was boiled under reflux for 5 h. After evaporation of the acetonitrile, the residue was extracted with diethyl ether and the solid material filtered off. Boiling with methanol gave yellow crystals, virtually insoluble in all solvents and with m.p. >350 °C. Acetonitrile and *N,N*-dimethylformamide were the best solvents but still the solubility was only ca. 1 mmol l^{-1} at ambient temperature. Anal: C, H, N, O. MS: *m/z* (M^+) = 720.

N,N,N′,N′-*Bis(tetramethylsuccinoyl)urea* (*T_2CO*). A 20 % solution of phosgene (1 ml; **WARNING:** very poisonous compound!) in toluene was mixed with a solution of 4.4 g Bu_4NT in 10 ml of acetonitrile. The solution was boiled under reflux for 15 min and then evaporated to dryness. Water and diethyl ether were added and the ether phase was separated and washed once with water. Evaporation gave a solid which was recrystallized from methanol, m.p. 160–170 °C (0.45 g, 69 %). ^{1}H NMR: δ 1.23 (s). ^{13}C NMR: δ 20.8 (CH_3), 47.9 (C), 142.0 (CO), 178.0 (CO in imide rings). MS (*m/z*): 336 (*M*). The compound gave a drawn-out reduction wave upon CV in acetonitrile/0.1 M Bu_4NPF_6 with E_{pc} = ca. −1.3 V vs. NHE.

N,N,N′,N′-*Bis(tetramethylsuccinoyl)oxamide* (*TCOCOT*). Oxalyl chloride (0.76 g, 5 mmol) was added to a solution of Et_4NT (2.83 g, 10 mmol) in 10 ml of acetonitrile. After a few minutes, the solution was evaporated to dryness. The solid residue was extracted by 100 ml of diethyl ether. After evaporation of the ether solution, 0.90 g of a white solid were obtained. It was recrystallized from methanol, m.p. 120–126 °C. MS: *m/z* (M^+) = 364.

1,3-Bis(tetramethylsuccinimido)acetone. Sodium (1.43 g, 62 mmol) was dissolved in 40 ml of absolute methanol whereupon tetramethylsuccinimide (9.6 g, 62 mmol) was added. The solution was evaporated to dryness. *N,N*-Dimethylformamide (60 ml) was added, followed by the dropwise addition of 1,3-dichloroacetone (4.0 g, 31 mmol). The mixture became purple–black immediately. After 1 h of boiling under reflux, the solvent was removed on a rotary evaporator. Diethyl ether (200 ml) was added and after filtration the ether solution was extracted with 6×25 ml of sodium carbonate solution (5 %) in order to remove TH and dark matter. According to GLC/MS analysis, the only volatile component in the ether extract was then TCH_2COCH_2T. Evaporation gave a solid residue (1.7 g), of which 1.0 g was subjected to flash chromatography on 50 g of silica. Elution with 30/70 ethyl acetate/light petroleum in 50 ml portions gave fractions 12–15 containing a total of 0.90 g of the title compound, m.p. 180–186 °C. ^{1}H NMR: δ 1.19 (s, CH_3), 4.34 (s, CH_2). ^{13}C NMR: δ 21.4 (CH_3), 27.1 (CH_2), 47.1 (C), 181.9 (CO in imide), 193.8 (CO). MS [*m/z*(%)]: 364 (*M*, 5), 196 (30), 182 (6), 168 (100).

3,4-Bis(tetramethylsuccinimido)hexane-2,5-dione (**7**). Bromine (1.6 g, 10 mmol) in 5 ml of acetonitrile was rapidly added to a solution of hex-3-ene-2,5-dione[19] (1.12 g, 10 mmol) in 25 ml of acetonitrile. The bromine colour immediately disappeared, and a solution of Bu_4NT in 35 ml of acetonitrile was added. The mixture was stirred at 50 °C until the reaction was over (GLC; after 1 h no further changes occurred). The solvent was evaporated off and water/diethyl ether was added. The ether solution was washed with 5 % aqueous sodium carbonate (3×15 ml) and water (10 ml). After being dried with sodium sulfate, the ether was evaporated and the residue was dissolved in boiling hexane/ethyl acetate (10/1). Treatment with decolourizing carbon gave a clear solution which was left at 0 °C over night. The crystals (60 mg) were filtered off, m.p. 145–147 °C, with formation of a new crystalline phase at ca. 150 °C and final melting at 175–180 °C. A second crop of somewhat sticky crystals (200 mg) was obtained after concentration of the mother liquor.

GLC/MS analysis revealed that the first crop was a single isomer of compound **7** and that the second was a mixture of both isomers of **7** (*meso/racemic*) and a third component, most probably the product of elimination of one TH from **7** (presumably the process also taking place during the melting-point determination referred to above).

First form of **7**, m.p. 145–147 °C: ^{1}H NMR: δ 1.196, 1.204 (2 s of 12 H each, ring-CH_3), 2.09 (CH_3), 5.46 (CH). ^{13}C NMR: δ 21.3, 21.5 (ring-CH_3), 26.9 (CH_3), 46.6 (C), 56.1 (CH), 181.7 (CO in imide), 198.5 (CO). MS [direct inlet, 50 eV; *m/z* (%)]: 420 (*M*, 1), 378 (4), 335 (10), 224 (11). GLC/MS gave *m/z* 265 (1) as highest peak (*M* − TH).

Second form of **7** (not isolated): ^{1}H NMR: δ 1.196, 1.204 (2 s of 12 H each, ring-CH_3), 2.03 (CH_3), 5.57 (CH). ^{13}C NMR: δ 21.1 (ring-CH_3), 26.7 (CH_3), 46.8 (C), 55.0 (CH), 182.0 (CO in imide), 200.0 (CO). GLC/MS gave *m/z* 265 (1) as the highest peak (*M* − TH). Elimination product [$CH_3COCH{=}C(T)COCH_3$, not isolated]: ^{1}H NMR: δ 1.25 (s, imide ring-CH_3), 2.40, 2.35 (2 s, CH_3), 7.04 (s, vinylic H). ^{13}C NMR: δ 21.2 (imide ring-CH_3), 25.8, 31.2 (CH_3), 47.8 (C in imide), 132.2 (C=C), 180.6 (CO in imide), 193.0, 195.8 (CO). MS: *m/z* 265 (*M*).

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