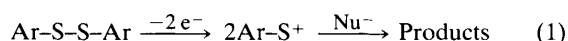# Anodic Oxidation of Di-*tert*-butyl Disulfide: a Facile Method for the Preparation of *N*-*tert*-Butylamides

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The electrochemical oxidation of di-*tert*-butyl disulfide is shown to correspond to a one electron process; at 1.3 V, one carbon–sulfur bond is cleaved yielding two intermediate species: the *tert*-butyl cation and the radical $Bu^tS-S^{\cdot}$; a Ritter reaction occurs with the cation when the solvent is a nitrile and the cation dimerizes into a tetrasulfide; at a more positive potential (1.9 V) the two carbon–sulfur bonds are cleaved giving Bu^{t+} and sulfur.

The electrochemical oxidation of organic disulfides, mainly diaryl disulfides, has been extensively investigated during the last two decades. Literature in the field is sometimes contradictory. Some authors believe that the oxidation process proceeds by a one electron transfer mechanism,[1–4] possibly leading to oligomers,[4] whilst other authors believe that a two electron transfer process is operative.[5] However, the anodic reaction can be understood as a symmetrical splitting of the –S–S– bond[6] and the postulated intermediate Ar–S$^+$ can react with nucleophiles (alkenes) to give products[1–5] as shown in eqn. (1).

$$Ar-S-S-Ar \xrightarrow{-2e^-} 2Ar-S^+ \xrightarrow{Nu^-} Products \quad (1)$$

Surprisingly, the behaviour of di-*tert*-butyl disulfide I has never been studied and it appears that the well known stability of both the *tert*-butyl radical and *tert*-butyl cation may induce different types of oxidative cleavage; this idea prompted us to investigate this kind of target molecule.

Voltammetry of I, run in acetonitrile containing tetraethyl-ammonium or lithium perchlorate (0.1 mol dm^{-3}) at a platinum working microelectrode exhibited an irreversible one electron step [+1.3 V *vs.* aq. saturated calomel electrode (SCE)] whatever the sweep rate value (up to 10^3 V s^{-1}). A second irreversible step (located at +1.9 V) appears by use of the recurrent sweep method, which has been identified as the di-*tert*-butyl tetrasulfide peak (Fig. 1).
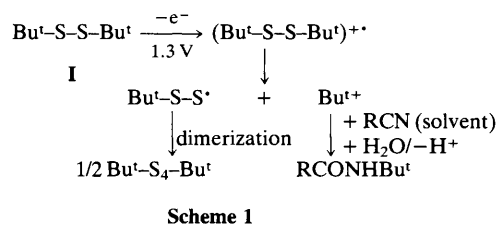
Table 1 Physical characteristics and spectral data of *tert*-butylamides prepared from di-*tert*-butyl disulfide

tert-Butylamides	Working potential /V vs. SCE	Solvent	M.p./°C	Yield (%)	IR v/cm⁻¹ (KBr or film)	¹H NMR (CDCl₃, SiMe₄) δ
BuᵗNHCOMe	1.3	MeCN	94 (lit.[7,8] 97)	93	v_{NH} 3280 $v_{C=O}$ 1655	1.36 (s, 9 H, Buᵗ), 1.95 (s, 3 H, MeCO), 6.80 (s, 1 H, HN)
BuᵗNHCOPh	1.5	PhCN	132 (lit.[7–10] 132)	96	v_{NH} 3310 $v_{C=O}$ 1627	1.48 (s, 9 H, Buᵗ), 6.00 (s, 1 H, HN), 7.25–7.90 (m, 5 H, Ph)
BuᵗNHCO-CH₂Ph	1.7	PhCH₂CN	108 (lit.[7] 115)	93	v_{NH} 3280 $v_{C=O}$ 1635	1.30 (s, 9 H, Buᵗ), 3.46 (s, 2 H, CH₂CO), 5.16 (s, 1 H, HN), 7.28 (s, 5 H, Ph)
BuᵗNHCO-CH₂CO₂Et	1.4	EtO₂CCH₂CN	Red oil	78	v_{NH} 3310 v_{C-O} 1035 $v_{C=O}$ 1735 and 1650	1.30 (t, 3 H, CH₂C*H*₃, *J* 7 Hz), 1.36 (s, 9 H, Buᵗ), 3.23 (s, 2 H, COCH₂CO), 4.20 (q, 2 H, OC*H*₂Me, *J* 7 Hz), 6.86 (s, 1 H, NH)
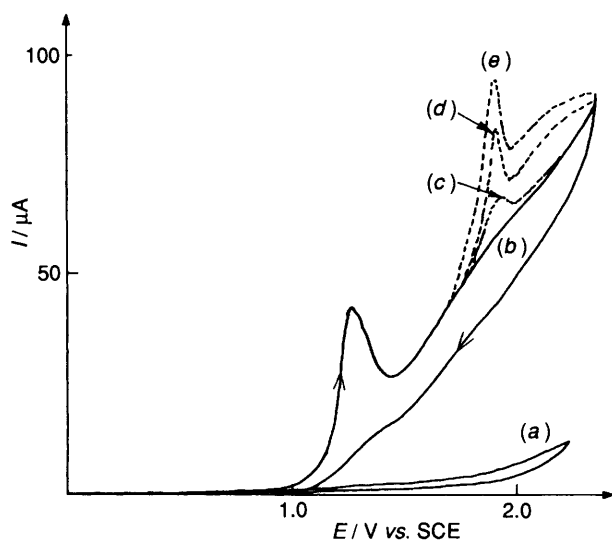
Fig. 1 Voltammograms of di-*tert*-butyl disulfide (9.17 × 10⁻³ mol dm⁻³) in MeCN–tetraethylammonium perchlorate 0.1 mol dm⁻³. Scan rate: 50 mV s⁻¹. (*a*) Without substrate, (*b*) first sweep, (*c*) second sweep, (*d*) third sweep, (*e*) fourth sweep.
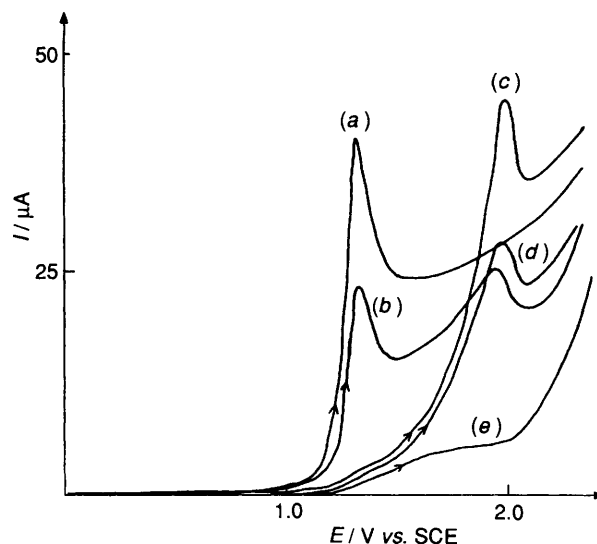
Fig. 2 Evolution of voltammograms during the course of coulometry of di-*tert*-butyl disulfide (9.36 × 10⁻³ mol dm⁻³) in MeCN–LiClO₄ 0.1 mol dm⁻³. Scan rate: 100 mV s⁻¹. First at fixed potential of 1.3 V: (*a*) 0 C, 0.0 F mol⁻¹; (*b*) 27.1 C, 0.5 F mol⁻¹; (*c*) 54.2 C, 1.0 F mol⁻¹; then at fixed potential of 1.9 V: (*d*) 81.3 C, 1.5 F mol⁻¹; (*e*) 108.4 C, 2.0 F mol⁻¹.

During potentiostatic microcoulometry, at a working potential of +1.3 V, a second peak appears and grows in size when treating one mol of electron per mol of **I** and then progressively vanishes until two mol of electron have been consumed when the potential has moved to +1.9 V (see Fig. 2).

Macroscale electrolyses were carried out in an H-type cell in a solution of acetonitrile–LiClO₄ (0.1 mol dm⁻³) using a platinum working electrode (*A* = 16 cm²). Using di-*tert*-butyl disulfide at a working potential of 1.3 V, two main products have been isolated and fully characterized: di-*tert*-butyl tetrasulfide† (96%) and *N*-*tert*-butylacetamide (93%) (yields are calculated according to the stoichiometry of Scheme 1). The formation of this latter compound is explained by a Ritter reaction between the intermediate *tert*-butyl cation and the nitrile group of the solvent. The tetrasulfide results *via* dimerization of the BuᵗS–S· intermediate radical, according to Scheme 1.

Buᵗ–S–S–Buᵗ $\xrightarrow[1.3\,V]{-e^-}$ (Buᵗ–S–S–Buᵗ)⁺·

I

Buᵗ–S–S· + Buᵗ⁺

dimerization | + RCN (solvent) | + H₂O/−H⁺

1/2 Buᵗ–S₄–Buᵗ RCONHBuᵗ

Scheme 1

If the working potential of the anode is shifted to 1.9 V, sulfur and *N*-*tert*-butylacetamide are isolated in almost quantitative yields, in agreement with the stoichiometry of Scheme 2, according to a global two-electron process.

Buᵗ–S–S–Buᵗ $\xrightarrow[1.9\,V]{-2e^-}$ 2 Buᵗ⁺ + 2 S

I | + 2 RCN | + 2 H₂O/−2 H⁺

2 RCONHBuᵗ

Scheme 2
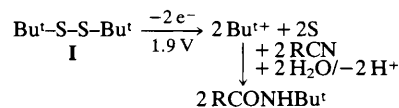
The reactivity of the transient cation was tested with several different nitriles as solvent: benzonitrile, benzyl cyanide and ethyl cyanoacetate, in all of which the di-*tert*-butyl disulfide peak is observed. Electrolyses at these potentials give high

† *Spectroscopic data* for di-*tert*-butyl tetrasulfide: yellow oil; IR (film) v/cm⁻¹ 2960, 2920, 1450, 1365; ¹H NMR δ (CDCl₃ + 2% SiMe₄, 60 MHz) 1.42 (s, Buᵗ). Satisfactory C, H and S analyses were obtained. MS *m/z* 242 (1.5, M⁺), 57 (100, Buᵗ⁺).

yields of N-tert-butylamides. Some physical characteristics are shown in Table 1.

In all cases the N-tert-butylamide is the sole product formed, besides sulfur, if electrolyses are carried out at fixed intensity (80 mA, current density 5 mA cm^{-2}).

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