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# Selective Bond Cleavage in RAFT Agents Promoted by Low-Energy Electron Attachment

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**Abstract:** *Radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization) has been successfully applied to generate polymers of well-defined architecture. For RAFT polymerization a source of radicals is required. Recent work has demonstrated that for minimal side-reactions and high spatio-temporal control these should be formed directly from the RAFT agent or macroRAFT agent (usually carbonothiosulfanyl compounds) thermally, photochemically or by electrochemical reduction. In this work, we investigated low-energy electron attachment to a common RAFT agent (cyanomethyl benzodithioate), and, for comparison, a simple carbonothioylsulfanyl compound (dimethyl trithiocarbonate, DMTTC) in the gas phase by means of mass spectrometry as well as quantum chemical calculations. We observe for both compounds that specific cleavage of the C−S bond is induced upon low-energy electron attachment at electron energies close to zero eV. This applies even in the case of a poor homolytic leaving group (·CH$_3$ in DMTTC). All other dissociation reactions found at higher electron energies are much less abundant. The present results show a high control of the chemical reactions induced by electron attachment.*

**T**he field of radical polymerization was revived during the 1990s with the development of methods that allowed for manipulation of molar mass and structure development during radical polymerization.[1] Reversible Deactivation Radical Polymerization (RDRP) techniques have enabled

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polymers with foreordained molar mass, low molar mass dispersity, and controlled structure and functionality of the chain-ends.[1] As these techniques developed from then on, varieties and advancements have been made that expanded the understanding of these polymerization methods and the capacity to utilize them for synthesis of a wide variety of polymers.[1] The radical reversible trapping or degenerative chain-transfer mechanisms exploited in RDRP methods ensure simultaneous development of most polymer chains and establish an equilibrium between propagating chains and dormant chains where the latter have a very long lifetime.[2,3] Atom-Transfer Radical Polymerization (ATRP)[4,5] and Reversible Addition-Fragmentation chain Transfer (RAFT) radical polymerization[6,7] represent the two most frequently utilized RDRP techniques.[1] RAFT is based on degenerative chain transfer mediated by a RAFT agent such as a dithio-carbamate, dithioester, trithiocarbonate, or xanthate.[8,9] A large variety of polymerizable monomers (such as (meth)-acrylates, styrene, vinyl esters, and even bio-derived monomers)[10,11] and solvents (like dimethylformamide or water) are compatible with RAFT polymerization. RAFT does not require the use of a catalyst and thus the need for purification after the polymerization reaction may be omitted.[12–15] However, RAFT polymerization requires a radical source to form propagating radicals from the monomer (see Figure 1). In the typical RAFT application, a thermal initiator is used as a radical source, which has the disadvantage of side reactions including the formation initiator-derived chain ends of the monomer, and irreversible chain transfer to initiator.[16]

Therefore, other methods are used to generate radicals directly from the RAFT agent and macroRAFT agent like photoinitiation,[17] metal-catalytic initiation[18] and redox chemistry.[19] These methods also enable enhanced spatio-temporal control over polymerization. For example, it was shown that RAFT polymerization can be initiated upon photoinduced electron transfer with chlorophyll as a photo-redox biocatalyst.[20] Recently, Lorandi et al.[21] and Strover et al.[22] successfully investigated the possibility to induce RAFT polymerization by electrochemical reduction of the RAFT agent. In such electrochemically mediated RAFT polymerization (eRAFT), the RAFT agent-derived radicals may act as initiator, see Figure 1. eRAFT should offer milder reaction conditions than standard thermally initiated RAFT polymerization, without the need for hazardous or expensive reagents.[8,21,22] In order to avoid direct electrochemical reduction of the CTA at the electrode, which otherwise may prevent polymerization due to irreversible consumption of the RAFT agent in side reactions, a mediated reduction may be used. Strover et al. used anthraquinone as an electro-
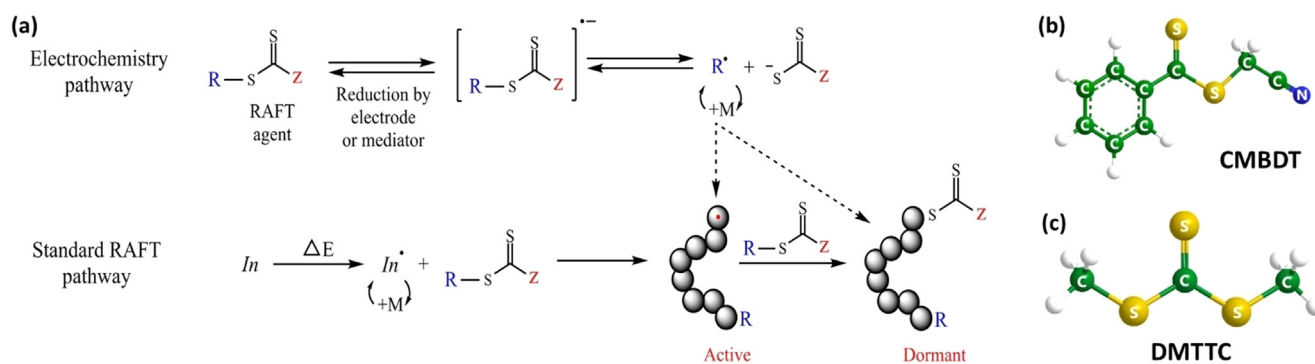
**Figure 1.** (a) Proposed reactions relevant for activation of RAFT agents by eRAFT ("Electrochemistry pathway") and standard methods ("Standard RAFT pathway") in solution which leads to the formation of a polymer (either in active or dormant status) upon addition of monomers M. (b) and (c) show the molecular structures of cyanomethyl benzodithioate (CMBDT) and dimethyl trithiocarbonate (DMTTC), respectively.

chemical mediator which allowed for the reduction of a trithiocarbonate RAFT agent in solution, avoiding unwanted electrochemical reactions at the working electrode, and thus initiating RAFT polymerization of methyl methacrylate.[22] Lorandi et al. reported the use of tetraphenylporphyrin as a mediator for eRAFT polymerization.[21]

As mentioned, reduction processes with subsequent chemical reactions are essential for several processes for initiating RAFT. In this gas-phase study we investigated the reactions induced by the attachment of a free low-energy electron to two different thiocarbonylthio molecules—a common RAFT agent (cyanomethyl benzodithioate, CMBDT, $C_9H_7NS_2$), and, for comparison, the model compound dimethyl trithiocarbonate (DMTTC, $(CH_3)_2CS$). We utilized a crossed electron-molecular beam setup with mass analysis of the anions as well as quantum chemical calculations. More details about the used methods are presented in the Supplementary Information. The carbonothioylsulfanyl molecules studied here -see Figure 1 for the molecular structures- belong to the classes of dithiobenzoates (CMBDT) and trithiocarbonates (DMTTC), respectively.

Electron attachment to a molecule is a resonance process that can be generally described as the first reaction step in equation (1),

$$e^- + AB \rightarrow AB^{\bullet-} \rightarrow A^{\bullet} + B^- \qquad (1)$$

where AB denotes the molecule and $AB^{\bullet-}$ the transient negative ion (TNI), which may have lifetimes up to the μs-time regime (required for detection in the present experiment). Equation (1) also shows one possible decay channel of the TNI, in which the two fragments $A^{\bullet}$ and $B^-$ are formed (dissociative electron attachment, DEA). This dissociation process competes with spontaneous electron emission by the TNI which limits its lifetime. Low-energy electrons may efficiently cleave molecular bonds via DEA, which is favoured by localisation of the excess charge at a highly electronegative moiety of a molecule, like for example halogen atoms of halogen-containing molecules[23] and the nitro group in radiosensitizers[24] as well as explosives.[25] In this first DEA study with one RAFT agent and one RAFT agent-like molecule we show that the molecular design of

these compounds allows the control of specific bond cleavages upon electron attachment. In addition, we observe that the molecular-bond cleavage relevant for RAFT initiation can be promoted by the capture of particularly slow electrons possessing a high attachment efficiency. Figure 2 shows all detected yields of anions formed upon electron attachment to DMTTC in an intensity map as a function of the initial electron energy and mass to charge ratio. As displayed in the Figure, we can observe a very weak amount of the parent anion at $m/z$ 138. The formation of this anion is restricted to electron energies close to zero eV. The detection of a parent anion in the present experiment implies that DMTTC has a positive electron affinity (EA), that is, the anionic state is energetically below the neutral state. Indeed, the quantum chemical calculations predict $+0.45$ eV for the EA of DMTTC which supports the experimental observation. Upon TNI formation, the kinetic energy of the attached electron and the electron affinity is deposited as excess energy in the internal molecular degrees of freedom of the TNI. Though DMTTC is a molecule of comparably smaller size, the
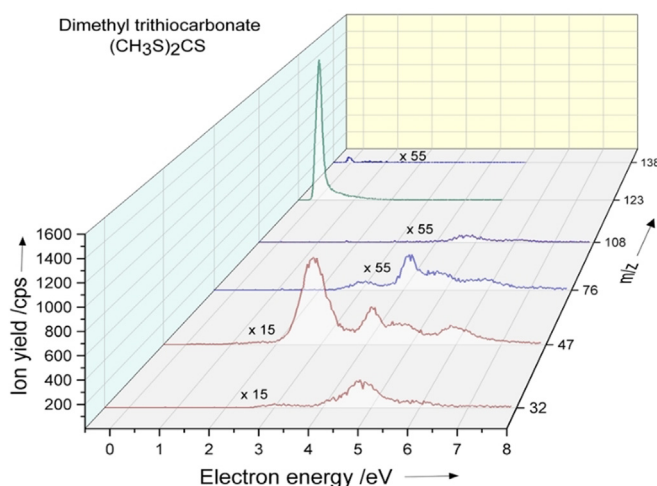


**Figure 2.** Intensity map of anions formed upon electron attachment to dimethyl trithiocarbonate, DMTTC. The map shows the intensity of $m/z$-selected anions as a function of initial electron energy between $\approx 0$ and 8 eV.

modest EA value enables detection of the parent anion at the electron energy of zero eV. The observation of a parent anion at higher electron energies is a priori omitted due to the excessive energy excess and can be obtained scarcely in gas phase experiments as for *para*-benzoquinone.[26]

By far the most abundant fragment anion is detected at $m/z$ 123, which corresponds to the loss of a methyl radical from the TNI of DMTTC [Eq. (2)],

$$e^- + DMTTC \rightarrow DMTTC^{\cdot-} \rightarrow CH_3SCSS^- + {}^{\cdot}CH_3 \qquad (2)$$

We note that the induced C–S bond cleavage also corresponds to the relevant one for free radical polymerization in solution (see Figure 1). The bond dissociation energy is 2.39 eV for the neutral molecule. We calculated the Gibbs free energy for the dissociation reaction of the parent anion leading to $CH_3SCSS^-$ and observed 0.16 eV, that is, the dissociation energy is much lower compared to the neutral compound. Since the EA of DMTTC is 0.45 eV, the DEA reaction (2) is overall exergonic by 0.29 eV. This predicted exergonic thermochemistry of the DEA reaction is also in agreement with the experimentally determined anion efficiency curve of $CH_3SCSS^-$, which shows a narrow peak at about zero eV, that is, no kinetic energy of the electron is required in order to cleave the molecular bond.[27] This observation also indicates the absence of a significant transition state barrier for this reaction channel. All other fragment anions observed experimentally for DMTTC ($S^-$, $CH_3S^-$, $SCS^-$ and $SCSS^-$) show resonances only at higher electron energies in the range between about 3 eV and 6 eV, see Figure 2. The corresponding anion yields are at least two orders of magnitude lower in intensity than for $CH_3SCSS^-$. The fragments $S^-$, $SCS^-$ and $SCSS^-$ require multiple bond cleavages in the molecule to form upon DEA. The present calculations predict endergonic DEA reactions in agreement with the experimentally obtained ion yields. $S^-$ may form by

cleavage of the C=S double bond or by two single C–S bonds. The corresponding predicted DEA thresholds are 2.15 eV and 3.56 eV, respectively. The experimental $S^-$ anion yield shows three peaks at 3.12, 4.83 and 5.75 eV. Since the first peak has the threshold at $\approx 2.4$ eV, we assign this peak to exclusive cleavage of the C=S double bond upon electron attachment. We also calculated the Gibbs free energy for other dissociation reactions, which lead for example to the anions $CH_3^-$ or $(SCSCH_3)^-$, see SI. These DEA reactions are also considerably endergonic with thresholds of 2.87 and 1.37 eV, respectively. Both anions were not observed within the detection limit of the experiment.

For CMBDT, we were not able to observe a parent anion upon attachment of a free electron, though the present quantum chemical calculations predict an even more stable anion compared to DMTTC. The computationally derived EA value of CMBDT is $+1.50$ eV. The non-observation of a parent anion despite a positive electron affinity may be explained by the higher excess energy released in the TNI of CMBDT, which leads to faster spontaneous electron emission or DEA. Indeed, the intensity map for CMBDT shown in Figure 3 indicates abundant fragment anion signal at $m/z$ 153, which is exclusively formed in a peak structure near zero eV. The ion signal can be assigned to the fragment anion $PhSCS^-$ (Ph = phenyl) formed in the DEA reaction [Eq. (3)],

$$e^- + CMBDT \rightarrow CMBDT^{\cdot-} \rightarrow PhSCS^- + {}^{\cdot}CH_2CN \qquad (3)$$
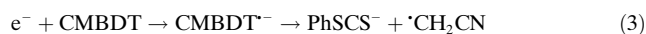
The formation of this fragment anion is accompanied by the release of the cyanomethyl radical $CH_2CN$. Thus, the bond cleavage favourable for RAFT applications is also predominantly induced upon electron attachment to CMBDT. The calculations predict a Gibbs free energy of 0.76 eV for this bond dissociation within the TNI while 1.84 eV is required to cleave this bond in the neutral molecule. Since the calculated EA of CMBDT is 1.50 eV, the DEA reaction (3) is exergonic by 0.74 eV in agreement with the experimental result of a zero eV peak. In contrast, the formation of the cyanomethyl carbanion $CH_2CN^-$ and neutral $PhSCS^{\cdot}$ has a predicted endogonicity of 0.44 eV. The anion signal of $CH_2CN^-$ is only weakly abundant close to this onset and instead shows the main peak at around 4 eV. The experimentally derived intensity map shown in Figure 3, just shows two additional anions, $CN^-$ and $S^-$. $CN^-$ exhibits peaks close to 2.5 eV and 6.5 eV. The intensity of the $CN^-$ anion is surprisingly low, given the high electron affinity of the cyano radical which represents a pseudohalogen (EA = $3.862 \pm 0.005$ eV derived experimentally[28]). The presently found weak abundance is in line with previous DEA studies with various nitriles, where the $CN^-$ channel was weakly abundant as well.[29] This result indicates that the direct excision of the cyanide anion is omitted in favour of a more indirect dissociation process with energy transfer into the C–C bond (vibrational predissociation), which was predicted earlier for nitriles.[29]

Like for DEA to DMTTC, we can observe the sulphur anion from CMBDT only at higher electron energies. The main peak in the $S^-$ anion yield is found at 5.38 eV, with the experimental onset at $\approx 2.8$ eV. The calculations indicate a large difference in the free energies, if $S^-$ is formed by
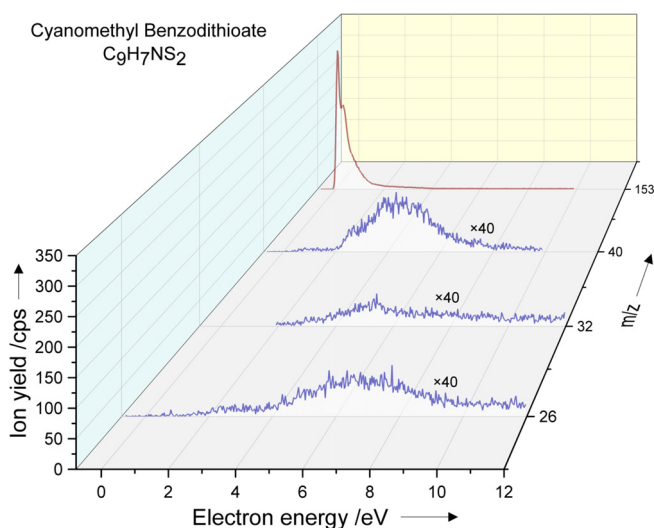


**Figure 3.** Intensity map of anions formed upon electron attachment to cyanomethyl benzodithioate, CMBDT. The map shows the intensity of $m/z$-selected anions as a function of initial electron energy between $\approx 0$ and 12 eV. The energy region below $\approx 2$ eV is omitted for $m/z$ 32 ($S^-$) due to the presence of yield from an impurity.

cleavage of the C=S double bond (2.62 eV) or two single C–S bonds (4.10 eV). Thus, the proximity of the former free energy value to the experimental threshold indicates S⁻ formation from this site. All other computationally investigated DEA reactions have Gibbs free energies of more than 0.99 eV, see SI. However, those anions (like for example, the carbon disulphide anion SCS⁻) were not observed in the experiment.

Comparing now the electron attachment characteristics derived for these two carbonothioylsulfanyl derivatives, the remarkable result is the boost of a specific DEA reaction with the same C–S bond cleavage which leads to the formation of the neutral R radical and the corresponding fragment anion. The measured intensity maps indicate that these reactions are at least two orders of magnitude more intense than other DEA reaction pathways. Close to the electron energy of about zero eV, the aforementioned C–S bond cleavage is even the exclusive reaction, which becomes also evident by the predicted thresholds for the DEA reactions, see Figure 4. RAFT agents are designed such that the bond to the radical-yielding R-group is comparably weak, with the aim that this bond is preferentially cleaved in order to (re)initiate the RAFT polymerization in solution.[12] The present results show that for the anionic system, the Gibbs energies are substantially reduced compared to the neutral systems, which should favour dissociation. However, the preferred selectivity of the bond cleavage in the molecules is even enhanced since the DEA reaction is induced by the attachment of an electron with (virtually) no kinetic energy. In such a case, the electron attachment cross section is inversely proportional to the square root of the electron energy[30] and thus the ion yields from exergonic DEA reactions without the presence of a barrier may become exceedingly intense. For all other DEA reactions observed, the electron affinity does not exceed the Gibbs energy of the dissociation reactions of the TNI.

Therefore, an electron with a kinetic energy of $> 2$ eV must be attached in order to induce these reactions. At such electron energies, the attachment cross section in finite compared to that at zero eV, which leads to the comparably low abundance of the other fragment anions observed.

In conclusion, we studied dissociative electron attachment to two carbonothioylsulfanyl derivatives containing a dithioester and trithiocarbonate group, respectively, and obtained predominantly C–S bond cleavage upon electron attachment to both compounds in the gas phase. This result can be explained by the subtle balance of dissociation energies and the electron affinity of the corresponding carbonothioylsulfanyl derivative. This balance leads to just one exergonic DEA pathway while all other DEA reactions are considerably endergonic. The exergonic reaction becomes additionally promoted since, due to the absence of a barrier, it can be induced at electron energies close to zero eV where the electron capturing efficiency has a maximum. Due to these favorable reaction properties related to the C–S bond cleavage, we expect that this fast simple bond cleavage will be also a relevant reaction in bulk solution, though in competition with secondary reactions,[31] which cannot be probed in the present gas phase study. Interestingly even though DMTTC and other unsubstituted primary and secondary alkyl trithiocarbonates are poor RAFT agents in polymerization. This is a consequence of methyl radical being a poor homolytic leaving group relative to most propagating radicals. The design of both the studied carbonothioylsulfanyl derivatives seems to be tailor-made for controlled bond cleavage upon electron attachment. The methyl radical is a good homolytic leaving group with respect to an electron. Therefore, we may expect an implication of the present results for the activation process in Single Electron Transfer (SET)-RDRP. While DMTTC is a poor RAFT agent, it is likely to be a good SET-RDRP initiator (methyl radical
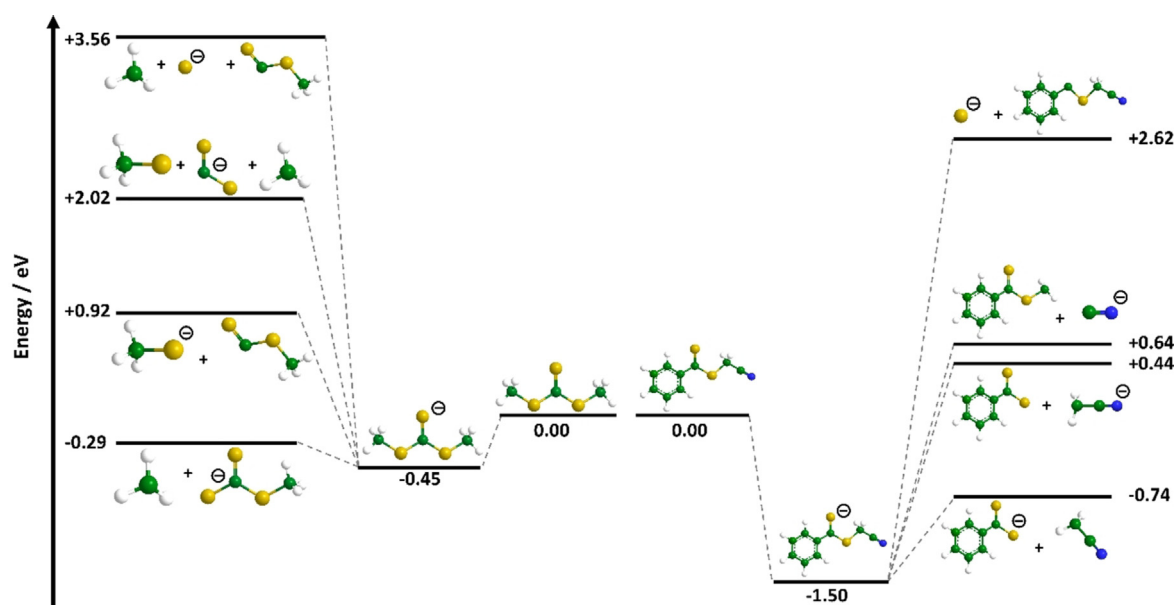


*Figure 4.* Thresholds (in eV) of the experimentally observed dissociation reactions of DMTTC, left, and CMBDT, right, calculated at M06-2X/Def2-TZVP level of theory. The weakest DEA channel for DMTTC, SCSS⁻ with a calculated threshold of 1.81 eV, is not shown.

will add rapidly to monomer) and the product dormant species after some propagation (propagating radical-TTC) should likely be a good RAFT agent. In addition, we anticipate that these results will be also relevant to initiation in photoinduced electron/energy transfer (PET-RAFT) that involves electron transfer to the RAFT agent.[32,33] Moreover, ionizing radiation may offer the release of low-energy electrons and subsequent DEA in solution.[34]

## Conflict of Interest

The authors declare no conflict of interest.

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