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COMMUNICATION

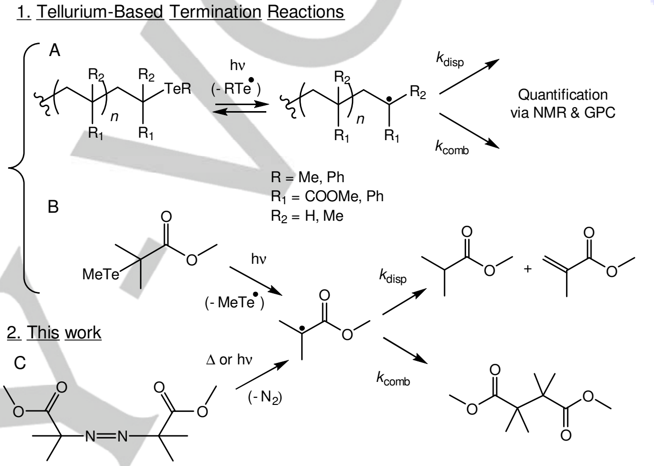
Catalyzed Radical Termination in the Presence of Tellanyl Radicals

Thomas G. Ribelli,[a] S. M. Wahidur Rahaman,[b] Krzysztof Matyjaszewski*,[a] Rinaldo Poli*[b],[c]

Abstract: The decomposition of the diazo initiator dimethyl 2,2'-azobis(isobutyrate) (V-601), generating the $Me_2C^{\bullet}(CO_2Me)$ radical, affords essentially the same fraction of disproportionation and combination in media with a large range of viscosity (C_6D_6, DMSO-d_6 and PEG 200) in the 25-100°C range. This is in stark contrast to recent results by Yamago *et al.* on the same radical generated from $Me_2C(TeMe)(CO_2Me)$ and on other X-TeR systems (X = polymer chain or unimer model; R = Me, Ph). The discrepancy is rationalized on the basis of an unprecedented $RTe^{\bullet}$-catalyzed radical disproportionation, with support from DFT calculations and photochemical V-601 decomposition in the presence of Te_2Ph_2.

The mechanism of radical termination is of fundamental importance in polymer chemistry. Bimolecular radical termination can occur via either disproportionation (Disp) or combination (Comb). Disp results in two chains, one with an unsaturated chain-end and one with a saturated one, while Comb gives a single chain following C-C coupling.[1] The respective amounts of Disp and Comb highly depend on the nature of the radical species. For example, styrenes[2] and acrylonitrile[3] radicals undergo predominately Comb while methacrylates undergo both Disp and Comb.[2b, 4] The termination of acrylates has been of intense, ongoing debate with contrasting evidence in favor of either Comb or Disp.[2a, 5]

Recently, Yamago *et al.* have put forth a few contributions towards the understanding of the radical termination mechanisms using a tellurium-mediated radical polymerization (TERP) system.[6] Various TERP macroinitiators, for instance poly(methyl methacrylate) (pMMA-TeR), poly(methyl acrylate) (pMA-TeR) and polystyrene (pSt-TeR) (R = Ph or Me) species with controlled molecular weight (MW) and narrow MW distribution, as well as corresponding low molar mass models (unimers), were synthesized and used as radical species precursors. The C-Te bonds were photolyzed, resulting in the pair of carbon- ($R_0\cdot$) and tellurium-based ($\cdot$TeR) radicals which then underwent spontaneous termination processes. The $\cdot$TeR radicals ultimately combine to form the RTe-TeR dimer, whereas the fate of the carbon-based radicals was investigated by NMR, SEC and MS to quantify the respective contributions of Disp and Comb, see Scheme 1 (A and B). Furthermore, the generation of radicals via photolysis allowed these termination reactions to be investigated under a wide variety of conditions by varying temperature and solvent.



Scheme 1. 1 (top): work using organotellurium initiators to generate carbon-based radicals from (A) TERP macroinitiators and (B) the unimer model of the pMMA-TeMe dormant species.[6] 2 (bottom): activation of the diazo compound V-601 to generate methacrylate radicals in the absence of tellurium compounds.

While the Disp/Comb ratio was as expected on the basis of previous literature reports for the $pMMA^{\bullet}$ and $pSt^{\bullet}$ radicals,[6a] it was surprisingly found that acrylate radicals resulting from a pMA-TePh macroinitiator terminate almost exclusively (99%) via Disp,[6b] in contrast with several other previous[5b, 7] and subsequent[8] reports. In the most recent contribution,[6c] it was shown that the product distribution depends on the reaction medium, a greater viscosity resulting in an increase of the Disp/Comb ratio. For example, 59% Disp was observed for the methacrylate unimer model compound $Me_2C(TeMe)CO_2Me$ at relatively low viscosity (η = 1.1 mPas), whereas this amount increased significantly to 94% at η = 84 mPas at room temperature. Even more glaring was the use of the styrene unimer model complex $CH_3(TeMe)CHPh$ in which case 14% Disp was observed at low viscosity (η = 1.1 mPas) and increased drastically to 99% at η = 84 mPas at room temperature. In order to rationalize these surprising results, Yamago and coworkers have put forth an "advanced collision model", which rests on the principle that Comb is more viscosity-sensitive than Disp, hence a viscosity increase would result in a more significant retardation of the Comb rate constant (k_c) than of the Disp constant (k_d).

We have also been interested in the termination mechanism of acrylates, particularly in the case when this is catalyzed by a transition metal complex such as certain Cu-based ATRP

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catalysts.[9] Initial studies have given strong indications that the Cu-catalyzed radical termination (CRT) overwhelmingly leads to Disp-type products in the ATRP of acrylates.[9b] In addition, a more recent analysis of the termination products of acrylate radicals led to the conclusion that pMA radicals spontaneously terminate predominantly by Comb, in contrast to the recent report by Yamago *et al.*[6b] These results, which will be reported separately,[10] led us to hypothesize that the presence of RTe$^{\bullet}$ radicals may promote Disp. In order to verify this hypothesis, it was necessary to first investigate the fate of radicals related to those of the investigation by Yamago *et al.*, but obtained in the absence of RTe$^{\bullet}$, and then to rationalize any observed differences.

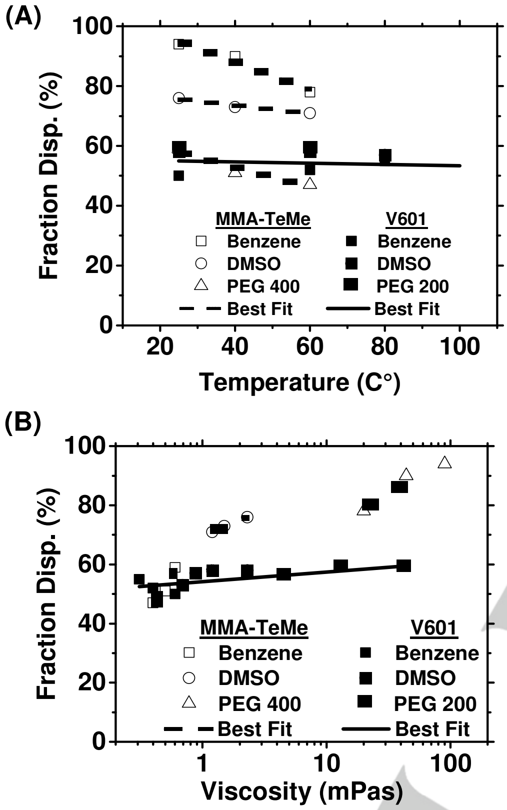
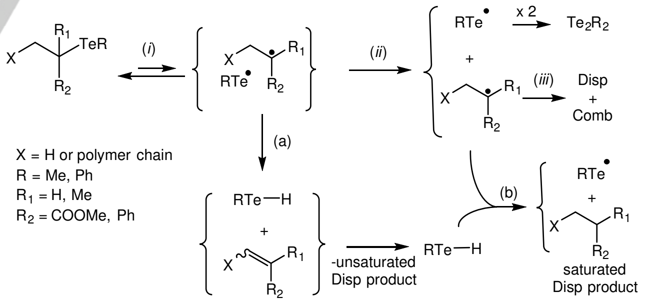


Figure 1. Fraction of disproportionation vs. (A) temperature and (B) viscosity for the isobutyryl radical in benzene (squares), DMSO (circles) or PEG 200/400 (triangles). Both the results obtained in this work from the V-601 diazo initiator (filled symbols) and those reported by Yamago *et al.*[6c] using the MMA-TeMe initiator (unfilled symbols) are shown for comparison. $[\text{V-601}]_0$ = 10 mM (DMSO & C_6D_6) or 100 mM (PEG 200) heated or irradiated for 24 hours. Colored figures can be seen in Figure S12.

We report here the use of the diazo initiator dimethyl 2,2'-azobis(isobutyrate) (V-601) as a radical precursor to study radical termination.[11] This compound, by either thermal or photochemical activation, yields a radical identical to one of those studied by Yamago *et al.*, see Scheme 1C. We show that the viscosity effects reported for the termination using the $Me_2C(TeMe)CO_2Me$ initiator are not observed in the absence of tellurium. Furthermore, introduction of Te_2Ph_2 in the photochemical V-601 decomposition in C_6D_6 increases the Disp/Comb ratio, indicating the action of PhTe$^{\bullet}$ as a Disp catalyst, which was further supported by DFT calculations We propose a simpler model, based on a viscosity effect on the radical diffusion away from the solvent cage, to rationalize the previously reported results.

The $Me_2C^{\bullet}(CO_2Me)$ radicals, generated from V-601, were allowed to terminate under conditions as close as possible to those used by Yamago *et al.* for the $Me_2C(TeMe)CO_2Me$ decomposition (for details, see the SI). The reactions were carried out in the same media, except for PEG 200 instead of PEG 400 because of better NMR spectral resolution (however, the viscosity range of these two solvents partially overlap), and in a wider temperature range (25-100°C). The % Disp and Comb obtained in all our experiments are collected in the Supporting Information (Table S1) and shown graphically in Figure 1 & S12. Examination of these results shows quite clearly that the temperature and the solvent nature have little effect, if any, on the relative proportions of Disp and Comb, thus questioning the validity of the previous proposed "advanced collision model".[6c]

A possible way to rationalize the different outcome of the two decomposition experiments is suggested by the analysis of the termination reaction as a stepwise process: (*i*) formation of the $Me_2C^{\bullet}(CO_2Me)$ radical and a second partner radical within a solvent cage, (*ii*) escape from the cage and (*iii*) termination by Disp and/or Comb. For V-601, both isobutyryl radicals needed for the termination events are formed within the same solvent cage, hence bimolecular termination may occur either within the solvent cage or after cage escape. For the tellurium-based system, on the other hand, cage escape is necessary for bimolecular radical termination between two isobutyryl radicals to occur. Thus, the observed difference in product distribution may result from the presence of side reactions between the $Me_2C^{\bullet}(CO_2Me)$ and tellanyl radicals within the cage.[12]



Scheme 2. Proposed mechanism for C-based radical disproportionation catalyzed by RTe$^{\bullet}$. (*i*) Radical pair generation; (*ii*) solvent cage escape; (*iii*) bimolecular radical termination

A possible side reaction is β-H abstraction[13] from the C-based radical by RTe$^{\bullet}$, resulting in RTe-H and an alkene (R = Me, Ph), as shown in Scheme 2, step (a). This process has been previously shown for Cr[14] and Co[15] complexes and can also be envisaged for any β-H-containing alkyl chains, such as pMMA, pMA, pSt and their unimolecular models. The RTe-H intermediate may then transfer the H atom to a second radical, yielding the

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saturated Disp product with regeneration of RTe$^•$ as shown in Scheme 2 step (b). Note that the tellanyl radical produced in step (b) may dimerize but may also induce disproportionation of additional radicals that have already escaped from their solvent cages.

The feasibility of this catalytic disproportionation has been analyzed by DFT calculations on both steps (a) and (b) of the catalytic cycle proposed in Scheme 2, using the same MeTe$^•$ and $Me_2C^•(CO_2Me)$ radicals of the experimental investigation presented in Figure 1 (see the computational details in the SI). The DFT results are summarized in Figure 2A. All optimized geometries and energies are collected in the SI. The unrestricted optimization of the MeTe$^•$ + $Me_2C^•(CO_2Me)$ radical pair, carried out under the broken symmetry approach (total spin S = 0) yielded a loose van der Waals minimum (**vdW1**), the shortest contact being 4.68 Å between the Te atom and one Me H atom. This adduct is slightly stabilized (-0.8 kcal/mol) relative to the sum of the two separate radicals on the gas-phase electronic energy scale (ΔE_{gas}), but destabilized on the Gibbs energy scale after corrections for dispersion and solvation in MeCN ($\Delta G_{D3,MeCN}$ = (+3.5 kcal/mol). In this adduct, each partner maintains its full spin density (1.000 for $MeCH^•(CO_2Me)$, of which 0.788 on the unsaturated C atom; -1.000 for MeTe$^•$, all on the Te atom). Step *a* is exoergic by 23.0 kcal/mol from the separated MeTe$^•$ + $Me_2C^•(CO_2Me)$ reagents. We failed to locate the transition state for this step (**TS1**) but our attempts prove that this must be located very near the **vdW1** minimum and that the barrier is nearly non-existent (see details in SI). Likewise, step *b* starts from a very loose van der Waals minimum (**vdW2**, shortest contact of 5.5 Å), slightly stabilized on the ΔE_{gas} scale (-0.7 kcal/mol) but destabilized on the $\Delta G_{D3,MeCN}$ scale (+0.6 kcal/mol) relative to the sum of the two separate species. The transformation is again exoergic through a very low energy and relatively "early" transition state **TS2** with the Te-H bond stretched to 1.738 Å (relative to 1.676 Å in **vdW2**), an H···C distance of 1.852 Å, and a low imaginary frequency of 177i cm^{-1}. In **TS2**, the spin density is still mostly localized on the C atom (0.657), though a significant amount is already transferred to the Te atom (0.200), whereas the H atom being transferred has a very low spin density of -0.036.

The above computations show the likelihood of the mechanism proposed in Scheme 2 for the MMA model radical. Thus, the same process may also take place for the other organotellurium reagents, in particular for the controversial case of the pMA$^•$ radical. This was further suggested by an analogous investigation on the PhTe$^•$/$MeCH^•(CO_2Me)$ radical pair, giving similar results (Figure 2B and further details in the SI). At this point, a reasonable interpretation of the results published in the contribution by Yamago and coworkers[6c] rests on the hypothesis that the solvent viscosity affects the rate of step (*ii*) (solvent cage escape). A viscosity increase slows down the radical diffusion away from the cage, providing a bias in favour of the RTe$^•$-catalyzed Disp. As the solvent viscosity is lowered and thus radical escape from the cage becomes more efficient, a greater contribution of Comb is observed for all radicals generated from organotellurium compounds, approaching the "true" uncatalyzed fraction of Disp to Comb.[6] The presence of "in-cage" radical reactions has previously been shown using alkoxy radicals.[12]

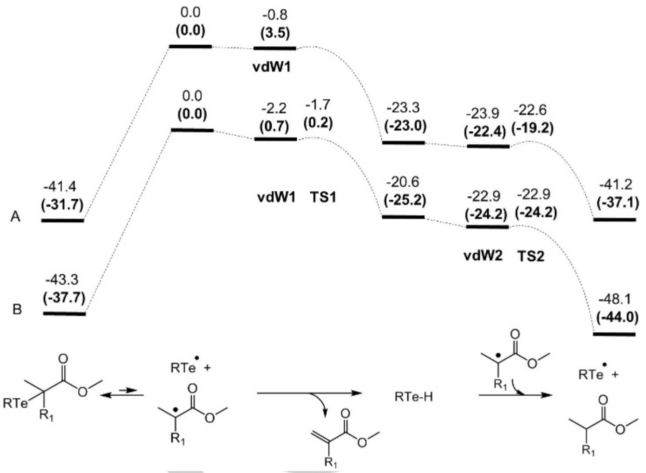

Figure 2. Results of the DFT calculations for steps *a* and *b* of Scheme 2. (A) R = Me, R_1 = Me and (B) R = Ph, R_1 = H. The gas-phase electronic energies (ΔE_{gas}) and the solvation- and dispersion-corrected free energies ($\Delta G_{D3,MeCN}$, bold characters in parentheses) are in kcal/mol.

It is also noteworthy that the PSt$^•$ radical, known to lead preferentially to Comb,[2] was also forced to dramatically shift preference to yield a Disp/Comb ratio of 97/3 when generated from PSt-TePh under very high viscosity conditions.[6c] We propose that this result can more easily be rationalized by the combination of a viscosity-dependent solvent cage escape and the PhTe$^•$-catalyzed Disp process, than by the "advanced collision model" proposed by Yamago *et al.*[6c]

In order to substantiate the proposed tellanyl radical-catalyzed disproportionation, the V-601 photochemical decomposition at room temperature in C_6D_6 was carried out in the presence of a tenfold excess of Ph_2Te_2, known to generate PhTe$^•$ under irradiation (see details in the SI). In this case, the putative PhTe$^•$-catalyzed disproportionation may only occur after the V-601-generated radical pair has escaped from the solvent cage. Indeed, the Disp/Comb ratio increased from 50/50 in the absence of PhTe$^•$ radicals to 68/32.

As a final remark, the Disp/Comb fraction obtained from organotellurium initiators appears to be much more skewed in favour of Disp for pMA than for pSt and pMMA compared to generally accepted Disp/Comb ratios. This could be related to the trend of RTe-alkyl bonds bond strengths (*i.e.* the energy associated to the homolytic C-Te bond cleavage, step (*i*) in Scheme 2). Radicals forming a weaker bond presumably have a greater recombination barrier (Hammond principle) and may be able to escape faster from the cage and thus be less susceptible to undergo the catalyzed Disp process. The DFT calculations support this view (see Table 1). For acrylate radicals, the occurrence of transfer reactions such as backbiting must also be carefully considered.[8, 10]

Table 1. Homolytic bond strength calculated by DFT for a variety of organotellurium systems.

Alkyl radical	$^•$TeR	ΔE_{gas}, kcal/mol	$\Delta G_{D3,MeCN}$, kcal/mol

$Me_2C^{\bullet}(CO_2Me)$	$^{\bullet}TeMe$	41.4	31.7
$Me_2C^{\bullet}(CO_2Me)$	$^{\bullet}TePh$	37.4	33.8
$MeCH^{\bullet}(Ph)$	$^{\bullet}TePh$	37.1	34.3
$MeCH^{\bullet}(CO_2Me)$	$^{\bullet}TePh$	43.3	37.3

In conclusion, the V-601 diazo initiator was used to thermally or photochemically generate isobutyryl radicals, which were allowed to undergo bimolecular termination. The resulting fractions of disproportionated (Disp) and combined (Comb) products were found to remain essentially unchanged over a wide range of temperatures and solvent viscosities, contrary to recent reports using organotellurium initiators. In-depth DFT studies demonstrated that a previously undiscovered $RTe^{\bullet}$ catalysed radical disproportionation reaction is viable, providing a likely interpretation of the previously published experimental results.[6] The proposed mechanism occurs via a β-H abstraction from the carbon-based radical forming an unsaturated chain end and a RTe-H intermediate. The latter species can then transfer the hydride to a second radical forming the saturated species and completing the catalytic cycle. At higher solvent viscosities, the alkyl/tellanyl radical pair diffuses more slowly out of the solvent cage and thus more time is available for the catalysed disproportionation to occur.

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Keywords: Radical termination • Tellanyl radical • Catalysis • V-601 • DFT calculations

References

[1] G. Moad, D. H. Solomon, *The Chemistry of free Radical Polymerization*, 2nd ed., Elsevier, Amsterdam, **2005**.

[2] a) C. H. Bamford, A. D. Jenkins, *Nature* **1955**, *176*, 78-78; b) Y. Nakamura, T. Ogihara, S. Yamago, *ACS Macro Letters* **2016**, *5*, 248-252.

[3] C. H. Bamford, R. W. Dyson, G. C. Eastmond, *Polymer* **1969**, *10*, 885-899.

[4] M. Buback, F. Gunzler, G. T. Russell, P. Vana, *Macromolecules* **2009**, *42*, 652-662.

[5] a) G. Ayrey, M. J. Humphrey, R. C. Poller, *Polymer* **1977**, *18*, 840-844; b) Z. Szablan, T. Junkers, S. P. S. Koo, T. M. Lovestead, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* **2007**, *40*, 6820-6833.

[6] a) Y. Nakamura, S. Yamago, *Macromolecules* **2015**, *48*, 6450-6456; b) Y. Nakamura, R. Lee, M. L. Coote, S. Yamago, *Macromolecular Rapid Communications* **2016**, *37*, 506-513; c) Y. Nakamura, T. Ogihara, S. Hatano, M. Abe, S. Yamago, *Chemistry-a European Journal* **2017**, *23*, 1299-1305.

[7] a) G. Odian, in *Principles of Polymerization*, John Wiley & Sons, Inc., **2004**, pp. 198-349; b) G. Ayrey, M. J. Humphrey, R. C. Poller, *Polymer* **1977**, *18*, 840-844.

[8] N. Ballard, S. Hamzehlou, F. Ruiperez, J. M. Asua, *Macromolecular Rapid Communications* **2016**, *37*, 1364-1368.

[9] a) K. Schröder, D. Konkolewicz, R. Poli, K. Matyjaszewski, *Organometallics* **2012**, *31*, 7994-7999; b) Y. Wang, N. Soerensen, M. Zhong, H. Schroeder, M. Buback, K. Matyjaszewski, *Macromolecules* **2013**, *46*, 683-691; c) H. Schroeder, M. Buback, *Macromolecules* **2014**, *47*, 6645-6651.

[10] T. G. Ribelli, K. F. Augustine, M. Fantin, P. Krys, R. Poli, K. Matyjaszewski, **submitted**.

[11] M. Yoshioka, T. Otsu, *Macromolecules* **1992**, *25*, 559-562.

[12] N. Chowdhury, A. Anoop, N. D. P. Singh, *Synthesis* **2012**, *44*, 1745-1754.

[13] A. A. Gridnev, S. D. Ittel, *Chemical Reviews* **2001**, *101*, 3611-3659.

[14] L. H. Tang, J. R. Norton, *Macromolecules* **2006**, *39*, 8236-8240.

[15] A. F. Burczyk, F. O'Driscoll, G. L. Rempel, *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3255-3262.

Entry for the Table of Contents

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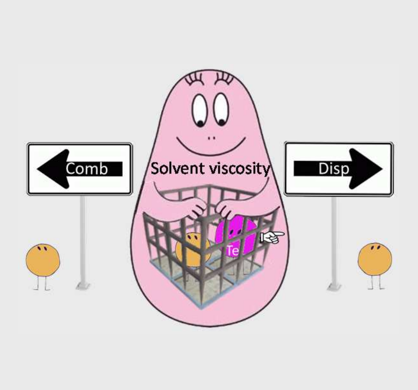
The bimolecular termination of $(CH_3)_2C^{\bullet}CO_2CH_3$ radicals generated from V-601 is essentially solvent and temperature independent, contrary to that of the same radicals generated from $(CH_3)_2C(TeMe)CO_2CH_3$; DFT calculations and V-601 photolysis in the presence of Te_2Ph_2 suggest an unprecedented Te-catalyzed disproportionation to account for these different results.



Thomas G. Ribelli S. M. Wahidur Rahaman Krzysztof Matyjaszewski, Rinaldo Poli**

Page No. – Page No.

Catalyzed Radical Termination in the presence of Tellanyl Radicals