



Addition of Br₂ to a triple bond: radical rather than ionic mechanism

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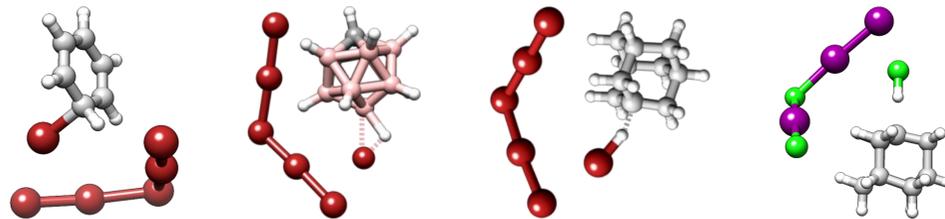
We have previously proposed a new type of electrophilic substitution reaction^{1,2,3,4} - "Cluster halogenation".

Unique features:

- No catalyst needed
- High kinetic order with respect to halogen
- Weak dependence of rate on temperature

Confirmed for Br₂ and ICl

Confirmed for aromatics, carboranes, adamantane:



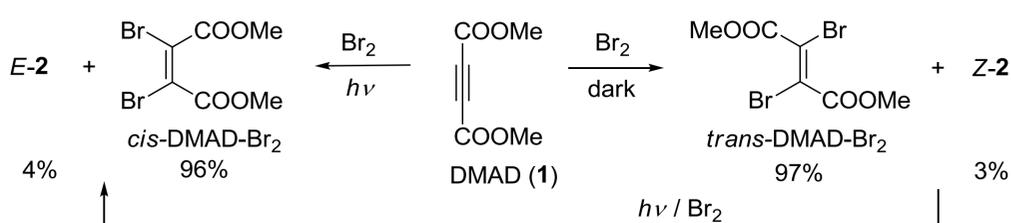
1. A. Shernyukov, A. Genaev, G. Salnikov, H. Rzepa, V. Shubin, Noncatalytic bromination of benzene: A combined computational and experimental study. *J. Comput. Chem.* **2016**, 37(2), 210–225, DOI:10.1002/jcc.23985.

2. A.V. Shernyukov, A.M. Genaev, G.E. Salnikov, V.G. Shubin, H.S. Rzepa, Elevated reaction order of 1,3,5-tri-tert-butylbenzene bromination as evidence of a clustered polybromide transition state: a combined kinetic and computational study. *Org. Biomol. Chem.* **2019**, 17(15), 3781–3789. DOI:10.1039/C9OB00607A.

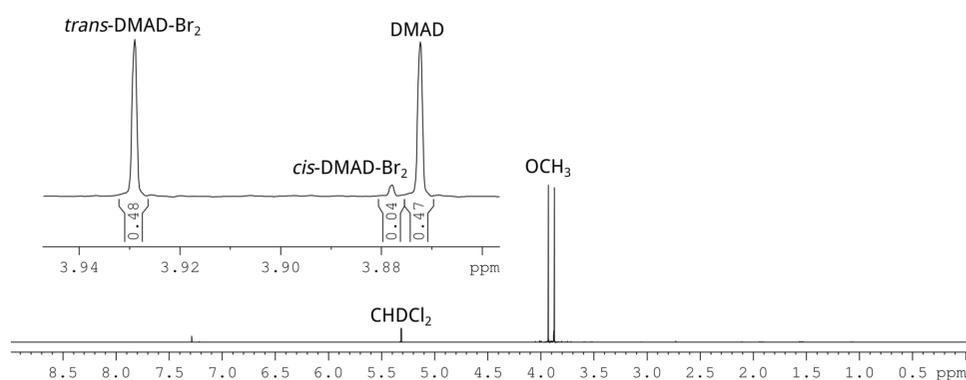
3. A.V. Shernyukov, G.E. Salnikov, D.A. Rudakov, A.M. Genaev, The Key Role of Anionic Bromine Clusters Facilitating Br Atom Insertion into the B–H σ-Bond Inorganic Chemistry, **2021**, 60, 5, 3106–3116. DOI: 10.1021/acs.inorgchem.0c03392

4. A. V. Shernyukov, G. E. Salnikov, V.I. Krasnov, A. M. Genaev Cluster halogenation of adamantane and its derivatives with bromine and iodine monochloride. *In print* **2022**

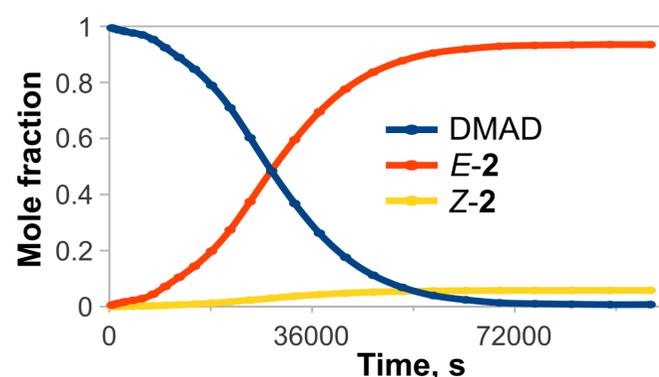
It is usually believed that the bromination of alkynes proceeds by an ionic mechanism, through bromonium ions. We tried to explore the possibility of Cluster halogenation mechanism for triple bonds, but we found that radical bromination proceeds even in the dark. We studied the bromination of some acetylenes, among which dimethyl acetylenedicarboxylate (DMAD) is unique in that it is brominated in bromine only by a free-radical mechanism.



Bromination kinetics are S-shaped. With the addition of a Br• radical scavenger, *tert*-butyl nitrite, the DMAD bromination reaction **does not proceed at all**, which indicates its radical nature even in **complete darkness**.

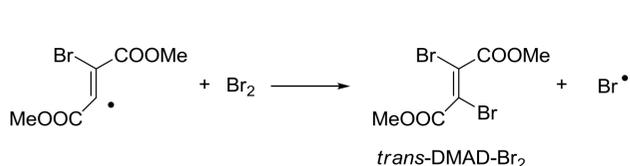
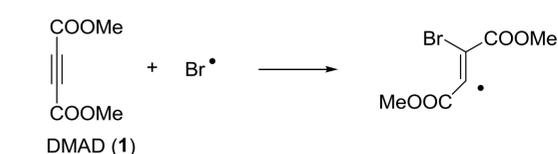


¹H NMR spectrum of the reaction mixture DMAD (0.05M) + Br₂ (4M) in CCl₄/CD₂Cl₂ after 8 h at 25 °C



Kinetics of the reaction DMAD (0.05M) + Br₂ (4M) in CCl₄/CD₂Cl₂ at 25 °C in dark

Free-radical chain reaction:



Bromine radical-catalyzed isomerization:

