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Mendeleev Commun., 2018, **28**, 190–191

Mendeleev Communications

EPR spectroscopy determination of the rate constants for addition of $[O_4S]^{\bullet-}$ radical anion to double bonds

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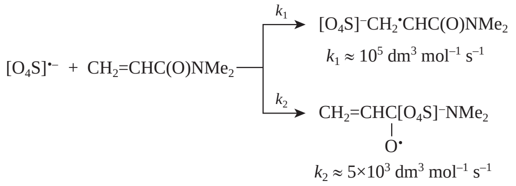
DOI: 10.1016/j.mencom.2018.03.027

The rate constants for addition of the radical anion $[O_4S]^{\bullet-}$ at C=C and C=O double bonds of *N*,*N*-dimethylacrylamine have been evaluated by the electron paramagnetic resonance technique.



The addition of free radicals to unsaturated bonds represents one of the general methods for the formation of new bonds, *e.g.* in telomerization, copolymerization and polymerization processes.[1–6] As for compounds with several unsaturated bonds differing in their physicochemical properties, the free radicals addition at different bonds and atoms should form different radicals, whose further transformations would drastically change the direction of the whole process. Therefore, the target generation of radicals is of undoubted interest, in particular, when homolytic reactions are initiated in a liquid phase. The fact of addition of sulfur-containing radicals at both carbon and oxygen atoms of carbonyl groups was discovered by preparative and spin trap electron paramagnetic resonance (EPR) methods.[7,8] The target application of such radicals in homolytic processes requires the knowledge of the rate constants for their addition to unsaturated bonds.

In the present study, we determined the rate constants for the addition of the $[O_4S]^{\bullet-}$ radical anion to *N*,*N*-dimethylacrylamide **1** by means of EPR. This reaction turned out to be suitable for measuring the rates of the radical addition to the carbon atom of the double bond and the carbon atom of the carbonyl group. Nitrosodurene (2,3,5,6-tetramethylnitrosobenzene) was employed as a spin trap (*cf.* ref. 9). The procedures for recording EPR spectra and processing experimental data were described earlier.[10]

In the course of the studies, spin adducts of oxygen (**6**) and carbon-centered (**5**, **7**) radical anions (Scheme 1) were identified by EPR analysis. Particle **8**, the spin-adduct of the initial $O_4S^{\bullet-}$ radical anion with the ArNO trap was also detected (Figure 1).

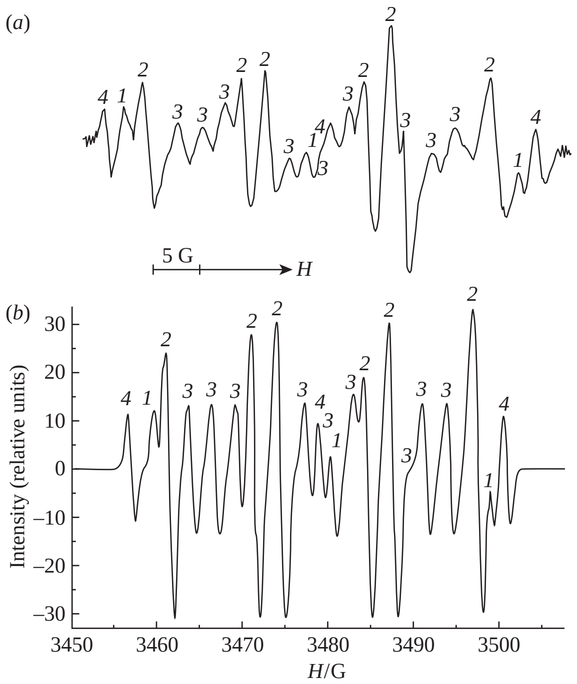
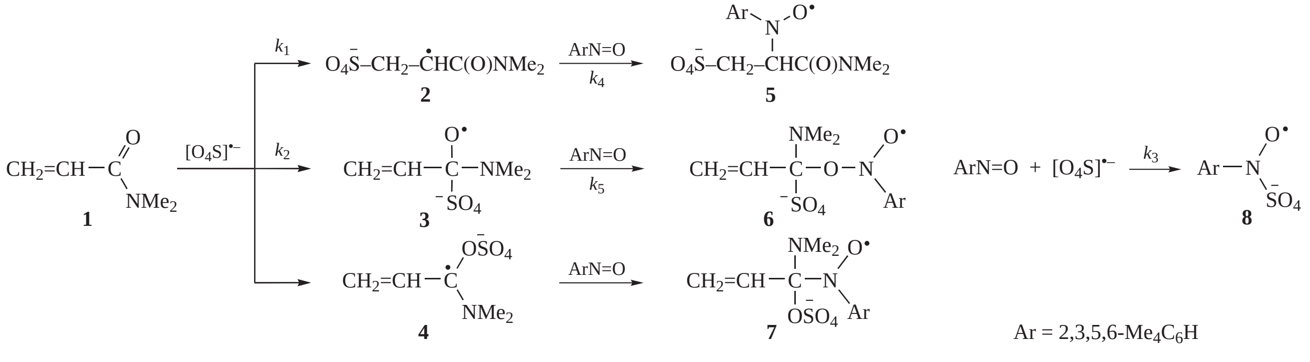


Figure 1 (*a*) Experimental and (*b*) simulated EPR spectra of the nitroxyl radicals formed due to the addition of $[O_4S]^{\bullet-}$ radical anion to *N*,*N*-dimethylacrylamide **1**: (*1*) $O_4\bar{S}N(O^\bullet)Ar$ **8**, (*2*) $O_4\bar{S}CH_2CH[C(O)NMe_2]N(O^\bullet)Ar$ **5**, (*3*) $CH_2=CH(NMe_2)C(O\bar{S}O_4)N(O^\bullet)Ar$ **7**, and (*4*) $CH_2=CH(NMe_2)C(\bar{S}O_4)$-$ON(O^\bullet)Ar$ **6**.



Scheme 1

Nitroxyl radicals **5–8** were characterized by the following hyperfine coupling (hfc) constants: $a_N = 13.1$ G, $a_H = 10.1$ G; $a_N = 22$ G; $a_N = 13.8$ G, $a_{N1} = 2.8$ G; $a_N = 19.2$ G, respectively. These values are close to the reported previously ones.[7]

Measuring the rate of formation of nitroxyl radicals **5**, **6** and **8** in the linear region of changing intensities of EPR signals on condition that $d[\mathbf{2}]/dt = 0$ and $d[\mathbf{3}]/dt = 0$, from the equations:

$$\frac{d[\mathbf{8}]}{d[\mathbf{5}]} = \frac{k_3[\mathrm{ArNO}]}{k_1[\mathbf{1}]}; \quad \frac{d[\mathbf{8}]}{d[\mathbf{6}]} = \frac{k_3[\mathrm{ArNO}]}{k_2[\mathbf{1}]}$$

with the known rate constant for the addition of the $[O_4S]^{\bullet-}$ radical anion to ArNO (k_3), we can determine the rate constant for the addition of $[O_4S]^{\bullet-}$ to carbon atoms of the C=C (k_1) and C=O (k_2) bonds.

Based on the measured rates of formation of spin adducts $d[\mathbf{8}]/d[\mathbf{5}] = 0.14$ and $d[\mathbf{8}]/d[\mathbf{6}] = 6.7$ (Figure 2) at the concentrations of compound **1** and ArNO of 5 and 0.001 mol dm^{-3}, respectively, the rate constants for the addition of the $[O_4S]^{\bullet-}$ radical anion to the carbon atom of the carbonyl group were calculated as $k_2 \approx 5\times10^3$ dm^3 mol^{-1} s^{-1} and to the carbon atom of the C=C bond as $k_1 \approx 10^5$ dm^3 mol^{-1} s^{-1} assuming that the rate constant k_3 for the addition of $[O_4S]^{\bullet-}$ to ArNO was 10^8 dm^3 mol^{-1} s^{-1}.[11,12] The k_1 value turned out to be an order of magnitude higher than those for the addition of radical $^{\bullet}CCl_3$ to the C=C double bonds in $CH_2{=}C(O)X$ (X = Me or OMe).[13] We failed to measure the rate of the formation of the nitroxyl radical **7**.

It is known that no principal grounds exist to distinguish between the reactivities of polymeric radicals and their low-molecular-weight analogues since the size of the particles does not influence their behavior in the addition processes. Based on published data,[14–16] the rate constant for the $[O_4S]^{\bullet-}$ addition to the carbon atom of a carbonyl group in dimeric products $O_4\bar{S}CH_2CH[C(O)NMe_2]CH_2CH[C(O)X][C(O)NMe_2]$ (X = Me, OMe) should be close to that for the addition of the dimeric radical $O_4\bar{S}CH_2CH[C(O)NMe_2]CH_2{}^{\bullet}CHC(O)NMe_2$ to a monomer (the rate constant for the addition of radical $CCl_3CH_2{}^{\bullet}CH[C(O)NC_4H_8]$ to $CH_2{=}CHC(O)NC_4H_8$ is 1.8×10^3 dm^3 mol^{-1} s^{-1}).[14]

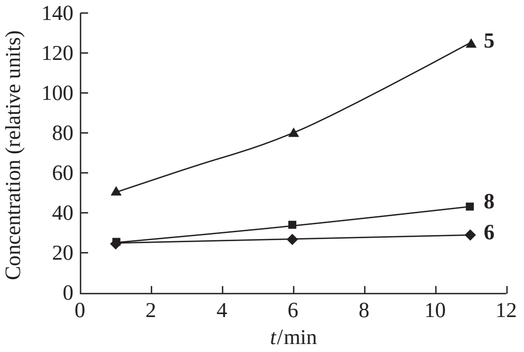


Figure 2 The time dependence of the concentrations of nitroxyl radicals **5**, **6** and **8**. For **6** and **8**, intensity of one line of triplet; and for **5**, intensity of one line of triplets of doublets.

Thus, one should take into account the possible addition of radicals to carbonyl double bonds when using sulfur-centered radicals for the initiation of polymerization, telomerization, and copolimerization of monomers bearing the carbonyl groups.

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Received: 11th July 2017; Com. 17/5306