

Methyl Methacrylate. Unusual Two-Electron Transfer Reaction and Carbanion Generation

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A single electron transfer (SET) mechanism is very common in many organic reactions. Such reactions are usually induced by organometallic complexes of transition metals or alkali metal complexes with arenes, radical anions being formed as reactive intermediates.^{1–3} The competition between electron transfer (SET) and S_N2 mechanisms has been observed in some organic syntheses, e.g., in the reaction of aromatic radical anions with alkyl halides and methane sulfonates.⁴ The theoretical aspects of single electron transfer in liquid solutions and in solids have recently been discussed.⁵

We have recently reported on the unusual two-electron transfer to β -lactones and styrene resulting in carbanions formation.⁶ Since carbanions are intermediates in many organic reactions, the novel route to carbanions via two-electron transfer and its utility in organic synthesis is of importance. Thus the question arises if two-electron transfer is a general mechanism operating also in the reactions of other compounds.

In this communication we present recent results on the unusual two-electron transfer to methyl methacrylate. Methyl methacrylate (MMA) is very versatile, reacting with alkylolithium,⁷ Grignard reagents,^{7,8} aluminum,⁹ titanium,¹⁰ and lanthanide¹¹ metallocenes. Since one-electron transfer (SET) to methyl methacrylate resulting in formation of a radical anion intermediate has been reported,^{2,3,11} the novel two-electron transfer reaction to MMA is discussed.

The discovery of macrocyclic ligands as crown ethers and cryptands^{12,13} which are able to complex alkali metal

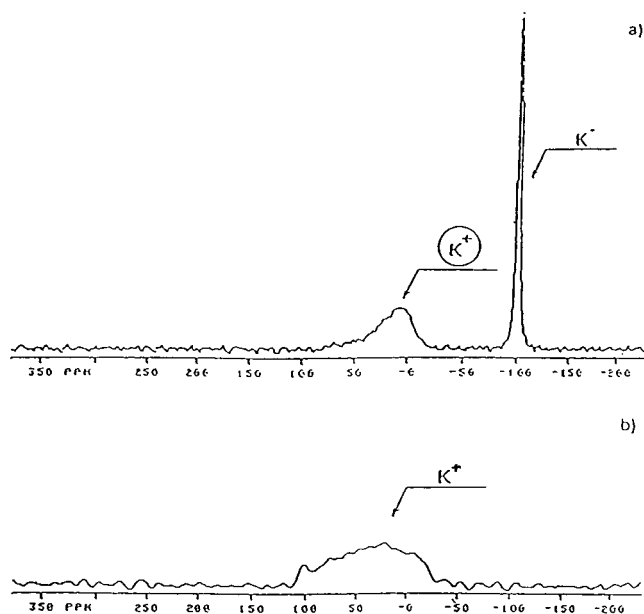


Figure 1. The ³⁹K NMR spectrum of the potassium complex with 18C6 (a) before the reaction with methyl methacrylate (b) after the reaction.

cations provided the possibility of alkali metal solubilization in aprotic solvents.^{14,15} The resulting alkali metal solutions contain complexed metal cations, solvated electrons, and metal anions. If the process of metal solubilization is performed according to the results of kinetic studies performed by us previously,¹⁶ the amount of electrons in the solution is negligible and metal complexes M⁺/crown, M⁻ (where M = K or Na, crown = 18C6) are the main products of alkali metal dissolution in an aprotic solvent.^{17,18} The alkali metal supramolecular complexes were found to induce two electrons toward electrophiles.⁶

The reaction of alkali metal supramolecular complex (K⁺, crown, K⁻) with MMA was performed in an aprotic solvent.¹⁹ It turned out that in the model reaction (methyl methacrylate:metal complex = 1:1) two electrons were transferred to the MMA forming dianion **2**, which underwent protonation instantly by the solvent and yielded a respective carbanion **3** (Scheme 1).

Thus the main products in the model reaction of MMA with the complex of potassium molar ratio 1:1, after

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(19) Reaction of methyl methacrylate with supramolecular complexes of potassium: The THF solution of 18C6 (0.2 mol/dm³) was kept in contact with potassium mirror for 15 min at temp 0 °C under inert gas atmosphere. Then, to the blue metal solution, filtered through glass frit, the equivalent amount of methyl methacrylate in THF solution was added till the blue color of the solution disappeared. After 5 min of stirring, protonation, methylation, or deuteration of the reaction mixture was performed by addition of methanol, iodomethane, or deuterated methanol (methyl-*d*₃ alcohol-*d*₁) in THF, respectively. The reaction products present in the discolorized solution after protonation, deuteration, or methylation were analyzed by GC-MS spectrometry.

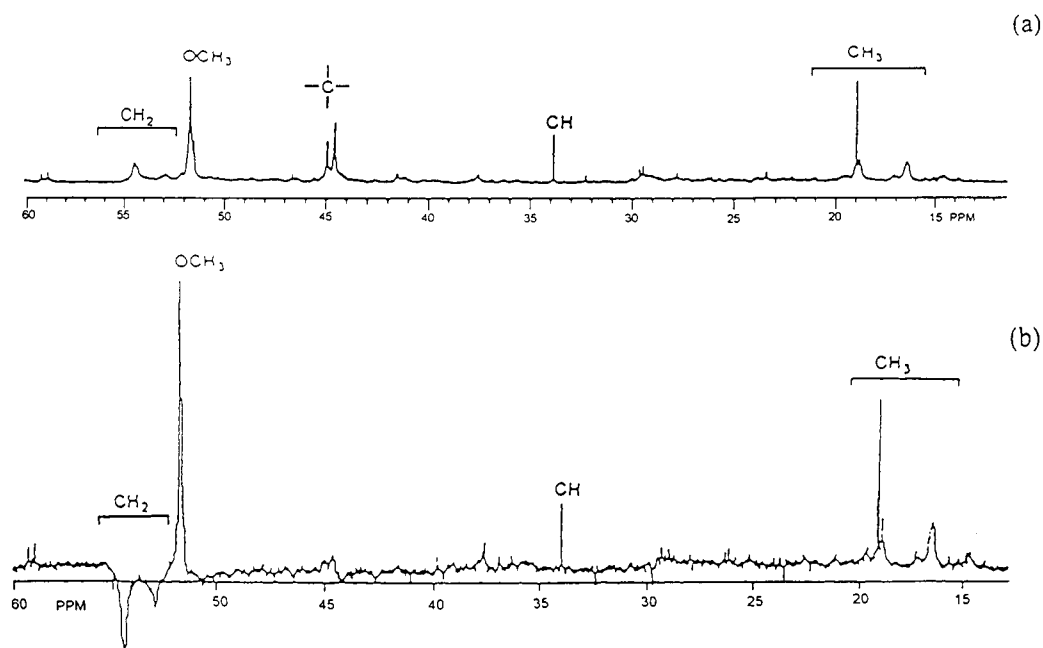
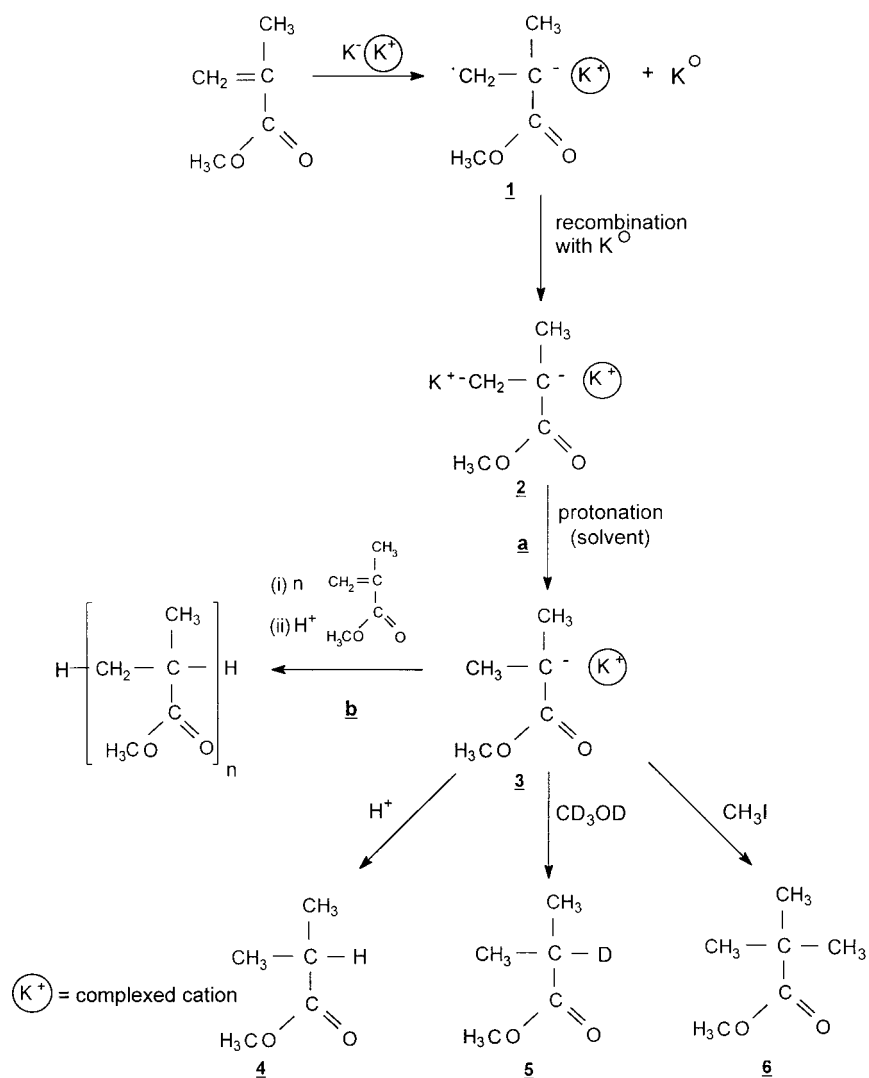


Figure 2. The ^{13}C NMR (a) and the ^{13}C DEPT (b) spectrum of MMA oligomers obtained in the presence of K^-/K^+ , 18C6 complex in THF, at 20 °C (MMA: K^- = 2:1).

Scheme 1



protonation by CH₃OH or deuteration by CD₃OD, are 2-methylpropanoic acid methyl ester **4** or respective deuterated compound **5** as evidenced by GC-MS analysis. The methylation of 1:1 reaction products by CH₃I, yields 2,2-dimethylpropanoic acid methyl ester **6** (Scheme 1a). The yield of these products is up to 80%.

Evidence on the transfer of two electrons was also provided by ³⁹K NMR. It was found that the signal of the potassium anion in the ³⁹K NMR spectrum of the metal complex disappeared after the reaction with methyl methacrylate, the resonance signal of cation becoming more intensive. It means that in this reaction the potassium anion, after the transfer of two electrons to the methyl methacrylate molecule, is converted into potassium cation (Figure 1).

The ¹³C NMR and the ¹³C DEPT spectra of oligomers, obtained in the reaction of MMA with K⁻/K⁺,18C6 complex in THF, molar ratio 2:1 or 3:1 (Scheme 1b), indicate the presence of a terminal methine proton, which can be formed as the end group due to two-electron transfer to the monomer MMA (Figure 2).

If MMA is present in excess in the reaction with alkali metal supramolecular complex the "living" MMA polymers are formed.

In summary, results on the two-electron reduction of MMA by potassium supramolecular complex are presented. The molar ratio of MMA to the complex is 1:1. Due to the transfer of two electrons by potassium anion to methyl methacrylate molecule carbanion of methyl methacrylate is formed. The latter being a strong nucleophile is able to react with electrophiles yielding respective functionalized methyl methacrylate. The MMA "living" polymers and block polymers can be also produced if the MMA monomer is present in excess.

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Supporting Information Available: Characteristic data of protonated, deuterated, and methylated products of the reaction of methyl methacrylate with 18-Crown-6 potassium complex. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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