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Laser-flash Photolysis of DMSO–Cl Complexes in Dimethyl Sulfoxide/CCl_4 Mixed Solvent

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DMSO–Cl complexes were produced by pulse radiolysis of mixtures of dimethyl sulfoxide (DMSO) and CCl_4 of various compositions, and photochemical reactions were studied by laser flash photolysis. The quantum yields of intramolecular hydrogen abstraction depend strongly on both solvent composition and additives.

Radiolysis of dimethyl sulfoxide (DMSO) in CCl_4[1] and CCl_4 in DMSO[2] results in the formation of transient DMSO–Cl complexes with an absorption maximum at 400 nm. In CCl_4 and other halocarbons, Cl atoms react with DMSO to yield the complexes.[1,3] The complexes are formed via two different paths in DMSO,[2] and the contributions of the two paths have been shown to depend on the CCl_4 concentration. The slow formation path is dominant for CCl_4 concentrations below 10^{-2} mol dm^{-3}; higher CCl_4 concentrations make the fast path more dominant. The fast formation of DMSO–Cl complexes has been shown to proceed by direct excitation of preassociated DMSO/CCl_4 pairs, based on laser-flash photolysis experiments.[4] The slow path has been ascribed to the reaction of $DMSO^+$ and Cl^- based on the results of pulse-radiolysis experiments of alkaline chlorides in DMSO. The latter path has been demonstrated in acidic aqueous solutions as well.[5] Since DMSO is a polar aprotic solvent with a relatively large dipole moment and CCl_4 is a nonpolar liquid, a wide range of polarities can be applied to solvents using mixtures of DMSO/CCl_4. This makes DMSO/CCl_4 mixed solvents suitable for producing DMSO–Cl complexes and for studying the effect of solvent polarity on the photolysis.

In the present study, successive electron and laser pulse irradiations were carried out by a combined pulse radiolysis–laser photolysis system with a time resolution of 10 ns as described previously.[6] Figure 1 shows kinetic traces observed at 400 nm by combined pulse radiolysis–laser flash photolysis of DMSO/CCl_4 mixtures (1/100, 1/1, and 9/1 volume ratio). The DMSO–Cl complexes were produced on irradiation with 50 ns pulses of 45 MeV electrons from a linear accelerator. Laser flash photolysis with 6 ns width pulses (355 nm) of a Nd:YAG laser was carried out at 1.5 µs after the electron pulse irradiation and resulted in rapid and permanent photobleaching of DMSO–Cl complexes. Actinometry was performed with deaerated benzene solutions containing benzophenone (1.0×10^{-3} mol dm^{-3}) and naphthalene (1.0×10^{-1} mol dm^{-3}). The extinction coefficient at the absorption maximum of DMSO–Cl complexes in CCl_4 was determined using the radiation chemical yield of the chlorine atoms in CCl_4 of 0.17 µmol J^{-1} as reported previously.[6b] The obtained extinction coefficient value of 7800 ± 50 dm^3 mol^{-1} cm^{-1} at 400 nm was applied to DMSO/CCl_4 mixtures, while the extinction coefficients at other wavelengths were determined based on the spectrum obtained with each mixture. The quantum yields of photobleaching were calculated to be 0.21, 0.13, and 0.065 for 1/100, 1/1, and 9/1 (v/v) DMSO/CCl_4 mixtures, respectively. All measurements were carried out at 16 ± 1 °C. The experimental uncertainty is ±10% for the quantum yields of photobleaching. Theoretical calculations gave bond dissociation enthalpy values of 103.0 and 98.5 kcal mol^{-1} for Cl–H and $CH_3S(O)CH_2$–H, respectively, indicating that the Cl atom can exothermically abstract hydrogen from DMSO to form $HCl + CH_3S(O)CH_2$.[7] Therefore, the observed photobleaching could be assigned to intramolecular hydrogen abstraction (reaction 1) as observed for methyl-substituted benzenes/Cl complexes.[6a,8]

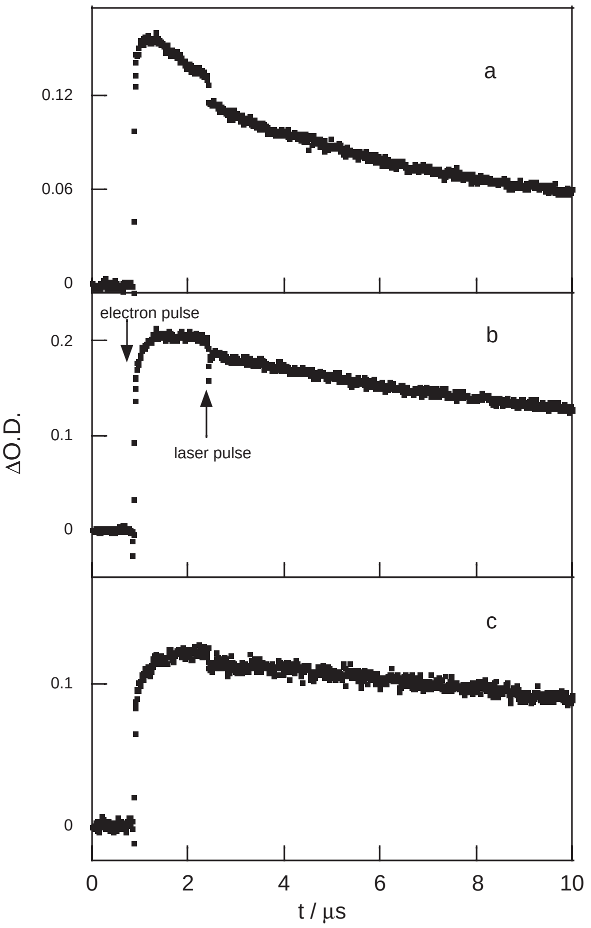

Figure 1. Kinetic traces observed at 400 nm by pulse radiolysis–laser flash photolysis (355 nm) of (a) 1/100, (b) 1/1, and (c) 9/1 (v/v) DMSO/CCl_4 mixtures.

$$CH_3S(O)CH_3\text{–}Cl \xrightarrow{h\nu} CH_3S(O)CH_2 + HCl \qquad (1)$$

The effects of benzene and 1-propanol observed for 1.1×10^{-2} mol dm^{-3} DMSO in CCl_4 are shown in Table 1. Ben-

Table 1. Effects of additives on the quantum yields of photobleaching of DMSO/Cl complexes produced on irradiation of 1.1×10^{-2} mol dm^{-3} DMSO in CCl_4

additive	concentration/mol dm^{-3}	quantum yield
none		0.24
benzene	1.13×10^{-1}	0.24
1-propanol	1.68×10^{-2}	0.35
1-propanol	6.72×10^{-2}	0.37

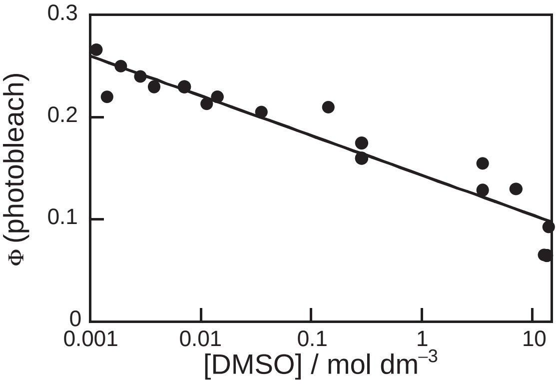

Figure 2. Quantum yields of photobleaching of DMSO–Cl complexes versus DMSO concentration.

zene exerts no influence on the quantum yield. However, addition of 1-propanol increases the quantum yield up to 150%. The concentration-independent increase of the quantum yields in the case of 1-propanol also strongly suggests the absence of intermolecular reactions. Therefore, it is possible that the photobleaching is exclusively due to intramolecular reactions, i.e., hydrogen abstraction by Cl atoms.

Since the dilute DMSO solution gave the highest quantum yield, the effects of DMSO in the concentration range 10^{-3}–2×10^{-1} mol dm^{-3} were investigated in detail. The photobleaching quantum yield increases up to 0.27 with DMSO concentration decrease as shown in Figure 2. The quantum yield of 0.093 obtained with 2×10^{-2} mol dm^{-3} KCl in DMSO is also plotted for neat DMSO (14.1 mol dm^{-3}).

The quantum yields of photobleaching decreased with increasing DMSO concentration. This result may evidence the effects of increasing solvent polarity with increasing DMSO concentration. However, the significant decrease at low [DMSO] (<0.1 mol dm^{-3}) cannot be accounted for by simple solvent polarity effects. DMSO is in the highly associated molecule category due to the anomalous concentration dependence of some of the physical properties of DMSO in various solvents.[9] The formation of a cyclic dimer has been suggested on the basis of infrared studies of DMSO in CCl_4.[10,11] Spectroscopic as well as thermodynamic[12–16] and nuclear magnetic relaxation[17] data support the formation of DMSO dimers at low concentrations. The DMSO dimer seems to predominate in the concentration range 0.02–0.3 mol dm^{-3}, and the value of its formation constant is estimated as 0.9 dm^3 mol^{-1}.[10] Thus, DMSO monomers exist predominantly in the concentration range below 8×10^{-3} mol dm^{-3},[3,10] and the significant decrease of the quantum yield at low [DMSO] may be induced by the association of DMSO. Previous pulse radiolysis experiments suggest a significant contribution of the ionic form $DMSO^+$–Cl^- for DMSO–Cl complexes.[2,18] Much larger contributions of the ionic form for the excited DMSO–Cl complexes could be expected. Since DMSO is known as a good solvator for the cations,[19] efficient stabilization of the excited complexes could lead to the decrease in the quantum yield.

Similar strong solvent effects on the rate constants have been reported for the reactions of ground state DMSO–Cl complexes with various compounds in DMSO/CH_2Cl_2 and DMSO/water solvents.[18] These effects have been ascribed to be partly due to the solvent polarity, but are mainly due to the specific solvation effect described above.

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